

RELATION OF COAL LIQUEFACTION CATALYST PROPERTIES TO PERFORMANCE

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INTRODUCTION

In March 1975, Amoco Oil Research, under contract with EPRI, began a three-year project on liquefaction catalysis (1,2). The specific purpose was to develop one or more superior catalysts for hydroliquefaction processes in advanced stages of development, such as the H-Coal process. The primary interest was in the conversion of coal to a clean-burning boiler fuel, low in sulfur and ash.

The hydroliquefaction of coal is a complex process which involves close interaction between the solubilized coal, hydrogen donor solvent, and catalyst. An improved catalyst for coal liquefaction must satisfy several requirements, but two key aspects are high initial activity for liquefaction-desulfurization and good aging characteristics.

Initial catalyst performance was determined in a batch test unit. A large number of catalysts, both commercially available and experimental, have been screened for initial performance. Catalysts selected on the basis of their physical and chemical properties as well as initial performance in the screening test were then subjected to continuous flow operation for approximately one week to determine their early deactivation behavior. Good initial performance of a catalyst may rapidly decline due to factors such as coking, sintering and metals deposition. Therefore a crucial aspect in developing a coal liquefaction catalyst is continuous operation for extended periods.

EXPERIMENTAL

Batch Screening Unit

The screening of catalysts for initial performance was carried out in a one-liter stirred autoclave. A mixture of 10 grams of catalyst (60-100 mesh granules, predried), 150 g coal and about 300 g liquefaction solvent was charged to the autoclave at ambient conditions. The coal was Illinois No. 6 from Burning Star Mine, ground to pass a 40 mesh screen. The solvent consisted primarily of mono-, di-, and trimethylnaphthalenes derived from petroleum refining and was essentially free of sulfur, nitrogen and oxygen. Pressure, hydrogen flow rate and mixing speed were set and reactor temperature was raised to 750°F in about 60 minutes. After

reaction at that temperature for 40 to 60 minutes, the reactor was cooled rapidly for removal of the reactor contents at ambient conditions. The test conditions are listed below.

Catalyst Screening Conditions

Catalyst	10g, 60-100 mesh
Coal, Illinois No. 6	150g
Solvent	300g
Pressure	2000 psig
Hydrogen flow rate	3 ft ³ /hr
Mixing speed	1800 rpm
Temperature (maximum)	750°F
Reaction time at 750°F	40-60 minutes

Product Workup and Analysis--Batch Unit

Evaluation of catalyst performance was based on the following procedure for separating liquid product from solid residue. The reactor contents were vacuum filtered and the filtrate segregated. Residual material was recovered from the reactor with benzene and washed through the filter cake. After additional washing with benzene, the filter cake and paper were Soxhlet extracted for 16 hours with benzene. The benzene solutions were combined and distilled to recover an extract that was added to the original filtrate. The final liquid which contains coal product, liquefaction solvent and a small amount of residual benzene was subjected to elemental analysis to determine product quality. The analysis was corrected for water and benzene present. The solid residue was dried at 160°C in a vacuum oven. A moisture and ash free conversion was defined on the basis of solid residue with the assumption that any change in the weight of the catalyst, which was not separated from the coal residue, would be of minor importance. Conversion, thus defined, has been referred to as benzene soluble conversion although, strictly speaking, the filtered product initially segregated in the product workup contained some converted material that is insoluble in benzene.

Catalyst Performance Indices--Batch Unit

Liquefaction conversion and the sulfur content of the coal liquid were used as the primary indicators of catalyst performance. The results obtained in the absence of catalyst provided the reaction baseline while Filtrol cobalt-molybdenum on alumina was selected as the reference for comparing initial catalyst performance.

Under otherwise constant conditions, conversion of coal to liquid product depends on reaction time and whether or not a hydrogenation catalyst is present. Simple reaction kinetics do not define the increase in conversion with increasing reaction time. Hence, some means other than the reaction rate constant is needed to assess catalyst activity. If the conversion obtained without added catalyst can be viewed as the result of noncatalyzed or thermal reaction, then at any given reaction time the increased conversion obtained with catalyst present is indicative of catalyst performance. The ratio of this increase to that obtained with the reference catalyst, Filtrol HPC-5, is defined as the conversion index.

There is also a corresponding decrease in product sulfur content as reaction time is increased. As with conversion, a desulfurization index can be defined as the decrease in product sulfur from the noncatalyzed baseline relative to that obtained with the reference catalyst at the same reaction time.

Continuous Testing Unit

The continuous pilot plant consists of three main sections as shown in the flow diagram (Figure 1). The first section called the feed module contains all equipment for feeding coal slurry and high pressure hydrogen. The center section which is the reactor module contains a 1-liter stirred autoclave and liquid product recovery system. The third module contains the gas let-down, metering and sampling facilities. The design conditions include a maximum working pressure and temperature of 4000 psig and 900°F. Once-through hydrogen is used in the catalyst activity test, but gas recycle has been provided. The once-through operation is preferred for aging tests since hydrogen pressure is maintained constant, independent of the light ends production.

The combined stream of coal slurry and hydrogen gas is continuously introduced into the bottom of the liquefaction reactor and reaction products withdrawn through a vertical overflow tube. A schematic of the reactor is given in Figure 2. Reactor holdup can be varied by changing the overflow tube height. A 60 cc catalyst charge is retained in a stationary annular basket. A specially designed blade impeller plus high agitation rate assures good mixing and contacting of the coal slurry with the catalyst.

Test Conditions--Continuous Unit

The nominal operating conditions used for catalyst testing in the continuous pilot plant are as follows:

Catalyst Test Conditions

Pressure	137 atm (2000 psig)
Temperature	427°C (800°F)
Hydrogen feed rate	170 liters/hr (6 scfh)
Slurry feed rate	400 gm/hr
Slurry concentration	20 wt%, -400 mesh coal (Ill. #6)
LHSV	1.33 gm coal/hr - cc cat
Residence time	48 minutes
Catalyst charge	60 cc
Mixing speed	1500 rpm

Product Workup--Continuous Unit

Product workup required considerable attention in this catalyst development program. To measure catalyst performance, one needs information on coal conversion and product quality. However, the information must satisfy certain requirements specific to the development program. This includes control of the aging test, a rapid measurement based on a small sample, and evaluation of the product quality, using a larger sample.

Coal liquids are normally characterized by solubility in a given solvent. Insolubles in coal product may be determined by different procedures which vary in extraction solvent; therefore, the solvent used defines conversion.

The product workup methods selected include two micro and one macro residue method using benzene and tetrahydrofuran (THF). Conversion based on the micro-benzene method (pressurized filtration using millipore cartridge filter) provides a quick index of product quality. Benzene soluble materials, such as asphaltenes and oils, represent the upgraded fraction of boiler fuel. Conversion based on the micro-THF method measures boiler fuel yield. Detailed evaluation of the liquid coal product requires a larger sample for boiling range determination and elemental analysis. The macro-THF residue method (Soxhlet extraction) is used for this purpose.

DISCUSSION

BATCH SCREENING RESULTS

Cobalt-Molybdenum Composition

The effect of varying the cobalt-molybdenum composition was examined to determine if the optimum catalyst composition for coal liquefaction might be different than that typically used in commercial desulfurization catalysts and to gain an indication of the impact of differences in catalyst composition on performance in the screening test. The study was made with two alumina supports having different surface properties--Cyanamid PA (ca. 300 m²/g, 60 Å) and Kaiser KSA Light (ca. 180 m²/g, 160 Å).

With both aluminas, conversion index increased rapidly up to about 10 wt% MoO₃ and then very slowly at higher molybdena contents (Figure 3). Both catalyst systems responded similarly to cobalt with the optimum lying between 2 and 4 wt% CoO. The Kaiser alumina, however, provided a more active catalyst than Cyanamid PA.

For desulfurization, the two supports were indistinguishable (Figure 4). Like conversion, desulfurization index increased rapidly up to about 10 wt% MoO₃ but then leveled off as molybdena content was increased further. The optimum cobalt content for desulfurization was also between 2 and 4 wt% CoO. However, desulfurization was much more sensitive than conversion when the cobalt content was reduced to zero.

Since catalysts made with two supports having different surface properties showed a similar relationship of performance to composition, it appears reasonable that a single composition of, say, 3 wt% CoO and 15% MoO₃ would be appropriate for studying the effects of the support on initial catalyst performance. Furthermore, small deviations from this composition should have only a minor effect on catalyst performance.

Surface Property Effects

The study on surface properties of cobalt-molybdenum catalysts focused primarily on the surface area and average pore diameter. These surface properties are considered important because the number of catalytic sites available depends on surface area and the accessibility of these sites is limited by the pore structure. Average pore diameter is an indicator of pore structure although the distribution of pore sizes may well be more important.

Consider, for example, the relationship of initial performance to the structural properties of the alumina supported catalysts. With respect to surface area, conversion index (CI) is relatively constant over a wide range while desulfurization index (SI) increases with increasing surface area (Figure 5). A corresponding disparity of performance is shown with respect to average pore diameter (Figure 6). The preferred average pore diameter for desulfurization appears to be smaller than for conversion.

These observations provide a basis for selecting catalysts for continuous testing. There is admittedly some scatter in the data which might be resolved by a closer look at such factors as pore size distribution. However, appropriate choices for determining the relation of activity maintenance to surface properties should include aluminas with average pore diameters in the range of 100 to 200 Å.

DISCUSSION-- CONTINUOUS TESTING RESULTS

The short-term aging behavior will now be discussed for a variety of catalysts tested in the continuous pilot plant. The main catalyst parameters we have focused on are surface properties, impregnating procedures, and type of catalytic metals.

Surface Properties and Impregnation Procedures

The effect of surface properties and impregnating methods was investigated by impregnating a series of alumina supports with cobalt and molybdenum. A phosphoric acid impregnating aid was used in some cases to adjust the acidity of the impregnating solution. Again, to facilitate data interpretation, surface area and average pore diameter were the two parameters used to characterize the surface properties, although the distribution of pore sizes should also be considered. The various CoMo on alumina catalysts tested are listed in Table I.

Table I. CoMo on Alumina Catalysts

<u>Catalyst ID*</u>	<u>Major Pores Å</u>	<u>APD Å</u>	<u>SA m²/g</u>	<u>PV cc/g</u>	<u>ABD g/cc</u>
HDS-1442 (ref)	30-110	58	323	.56	.57
KSA-LP	50-250	105	195	.70	.59
Grace-100UP	60-200	118	140	.54	.69
Grace-200UP	110-300	187	78	.44	.75
Grace-100U	60-200	122	167	.59	.68
Grace-200U	110-300	202	92	.52	.73

*U: unimodal; P: phosphorus addition

Referring to Figure 7, we compare liquefaction conversion for the various catalysts to the reference catalyst, HDS-1442A. First of all, the larger pore catalyst, Grace-200UP, results in higher conversion than the smaller pore version, Grace-100UP. The catalyst based on Kaiser KSA-LP alumina exhibits a rapid decline in activity even though its APD is around 100 Å. Closer inspection of the pore size distribution reveals that the KSA-LP alumina has a broad distribution of pore sizes.

The elimination of the phosphoric acid impregnating aid causes an upward shift in conversion for the catalyst prepared with Grace-100U alumina. However, no improvement was observed on the large pore Grace-200U alumina by eliminating the phosphoric acid. Therefore the best liquefaction performance is achieved with an alumina having an APD and surface area of 100 Å and 200 m²/gm, respectively. Furthermore, a phosphoric acid impregnating aid is detrimental to the liquefaction performance.

Desulfurization performance of the catalysts was evaluated by monitoring the sulfur content of the resid fraction (975°F+) of the coal liquid product. Referring to Figure 8, the lowest sulfur level was achieved with the catalyst prepared on Grace-100U alumina. We again conclude that the Grace-100U alumina gives the best overall performance.

Alternate Catalytic Metals

A series of catalyst tests to explore the effects of varying hydrogenation and cracking activity was also performed. Alternate hydrogenation metals tested include Ni-W, Ni-Mo, Ni-Mo-Re, all supported on the small pore Grace 100 alumina. Cracking activity was increased by impregnating the alumina with silica prior to impregnation with the catalytic metals. The specific version tested was a Ni-Mo on a silica promoted alumina. Inspections for the catalysts employing alternate catalytic metals are listed in Table II.

Table II. Catalyst Inspections--Alternate Hydrogenation Metals

<u>Catalyst</u>	<u>Composition</u>	<u>APD Å</u>	<u>SA m²/g</u>	<u>PV cc/g</u>	<u>ABD g/cc</u>
HDS-1442A	3.1 CoO-13.2 MoO ₃	58	323	.64	.57
Grace-100U	2.9 CoO-16.8 MoO ₃	122	167	.59	.68
NiW-100U	3 NiO-25 WO ₃	118	140	.52	.75
NiMo-100U	2.0 NiO-16.2 MoO ₃	119	163	.62	.67
NiMoRe-100U	3 NiO-16 MoO ₃ -2.3 Re	113	158	.58	.69
NiMo-100U/Si	3 NiO-16 MoO ₃	---	---	---	.66

Benzene soluble conversion is plotted against time on stream in Figure 9 for all of the catalysts in Table II. Compared to the cobalt-molybdenum catalyst (Grace-100U), both NiMo and NiMoRe gave lower benzene soluble conversion and faster decline rates. Addition of rhenium to NiMo had little effect. The more acidic support, silica promoted alumina,

did not improve performance of nickel-molybdenum. The increase in benzene soluble conversion of NiMo catalysts over the reference HDS-1442A catalyst can probably be explained by more favorable surface properties and higher density. Nickel-tungsten gave the lowest benzene soluble conversion which confirmed previous batch screening results.

CONCLUSIONS

Effective tests have been developed to evaluate coal liquefaction catalysts and relate their performance to catalytic properties. Initial performance in the batch unit was related to metals loading of cobalt and molybdenum and surface properties, specifically average pore diameter and surface area. Aging behavior of liquefaction catalysts was established for several catalysts in a continuous pilot plant unit. Surface properties had the most pronounced effect on aging performance; type of catalytic metals appeared to be a secondary effect.

REFERENCES

1. Brooks, J. A., Bertolacini, R. J., Gutberlet, L. C., Kim, D. K., "Catalyst Development for Coal Liquefaction," Electric Power Research Institute First Annual Report AF-190, February, 1976.
2. Bertolacini, R. J., Gutberlet, L. C., Kim, D. K., Robinson, K. K., "Catalyst Development for Coal Liquefaction," Electric Power Research Institute Second Annual Report, October, 1977.

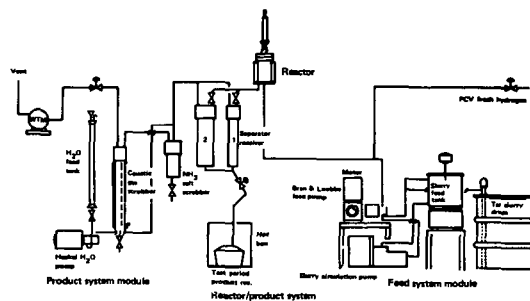


Fig 1 Unit flow diagram

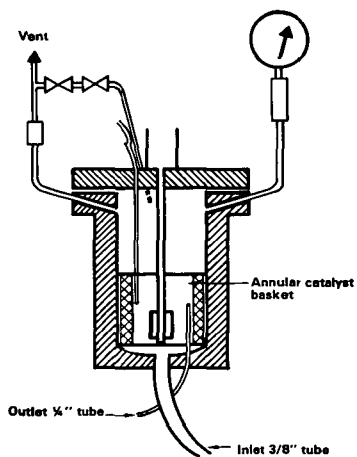


Fig 2 Liquefaction reactor

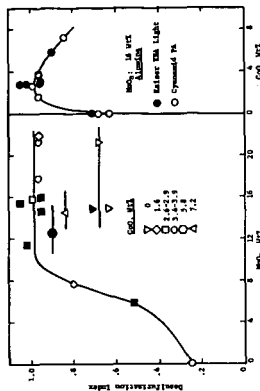


Figure 4. Effect of Catalyst Composition on Desulfurization Index

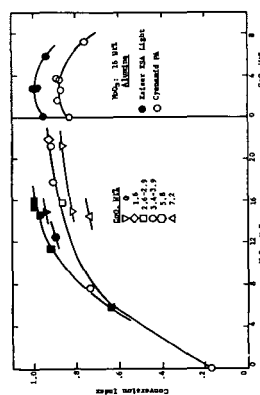


Figure 3. Effect of Catalyst Composition on Conversion Index

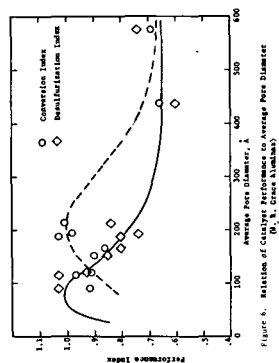


Figure 6. Relation of Catalyst Performance to Average Pore Diameter (N. H. Green Alundum)

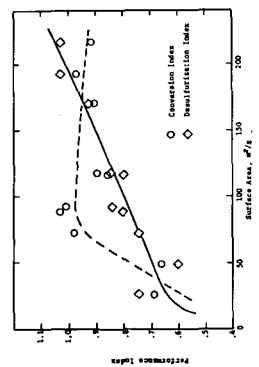
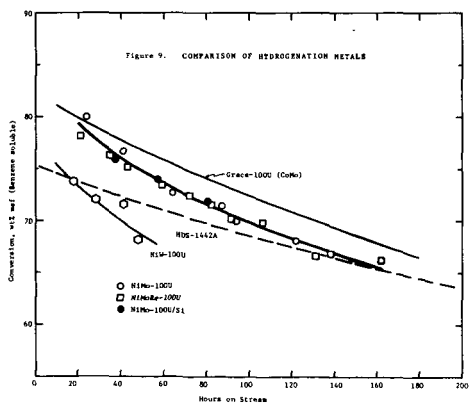
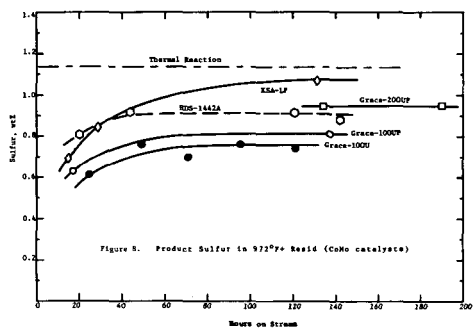
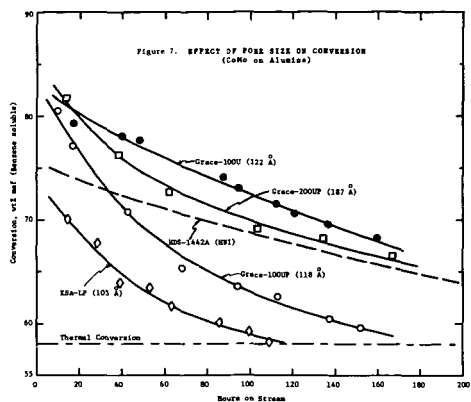


Figure 5. Relation of Catalyst Performance to Surface Area (N. H. Green Alundum)



BATCH SCREENING OF COAL LIQUEFACTION CATALYSTS
WITH A FALLING BASKET REACTOR

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The Harshaw Chemical Company and Battelle Columbus Laboratories have been studying coal liquefaction catalysts in a joint program sponsored by the Dept. of Energy. Its objective is the development of catalysts of improved life and selectivity for direct liquefaction processes.

Harshaw's specific objective is to identify catalysts of superior activity and selectivity, i.e. those that most efficiently use hydrogen in forming coal liquids with low heteroatom content. These will then be tested by Battelle for longer term aging characteristics. This paper is a report of progress with about half of the planned screening tests completed.

Experimental System

The test system, diagrammed in Figure 1, is based on an Autoclave Engineers 1-liter Magnedrive reactor and is designed to run whole formed catalysts in an environment of coal slurry with continuous hydrogen flow.

Illinois No. 6 coal from Consolidation Coal Company's Burning Star Mine No. 2 was analyzed as follows after grinding and drying.

	<u>Wt %</u>
Moisture	1.3
Ash	12.0
Carbon	68.3
Hydrogen	4.7
Nitrogen	1.2
Sulfur	3.2
Oxygen (by diff.)	9.3

The coal is charged to the reactor as 30% MAF coal in a vehicle. Two vehicles have been used. The first is a "heavy oil" cut of a coal tar from Koppers Co. Analyses of this vehicle and the coal are shown below.

	<u>Wt % Components</u>	
	<u>Coal</u>	<u>Heavy Oil</u>
Oil	1.0	76.9
Asphaltenes	0.3	22.8
Pre-asphaltenes	7.8	} 0.3
Residue	90.9	
	<u>100.0</u>	<u>100.0</u>
% Sulfur	3.2	0.44
% Nitrogen	1.2	0.96

In the second series of runs the vehicle is tetralin. Run conditions for the two series are as follows:

Vehicle	Heavy Oil	Tetralin
Pressure, psig	4000	2500
Temperature, °C	425	425
Activation in H ₂ /H ₂ S, hr	1.5	1.5
Thermal Reaction Period, hr*	0.5	1.0
Catalytic Reaction Period, hr	2.0	2.0
Inlet H ₂ Flow, SCFH	5	10
Catalyst Charge, cc	25	25
Wt Coal, g	188	162
Wt Vehicle, g	355	306
Volume of Slurry, cc	471	471

*After heatup to 425°C

Falling Basket Reactor

It is desirable that a catalyst screening test simulate continuous operating conditions as far as possible. In this case, five requirements were set in advance.

1. Batch operation for rapid screening.
2. Pre-activate the catalyst in situ with H₂/H₂S.
3. Use formed catalyst (tablets and extrudates) rather than powder.
4. Avoid contact of catalyst with slurry during heatup.
5. Separate thermal from catalytic conversion experimentally.

The Falling Basket Reactor, illustrated in Figure 2, was developed to meet these requirements. With this device, the catalyst is suspended in the gas phase during the initial stages of the run, then lowered into the liquid for the catalytic reaction portion. Catalyst (25 cc) is loaded in the four arms of the basket assembly which moves along a grooved sleeve attached to the agitator shaft. In operation the basket is held at the top of the shaft by a horizontal notched groove as long as the shaft is rotated at a constant RPM. (Rotation speed was set at 300 RPM after a preliminary mixing study.) When rotation is stopped and momentarily reversed, the basket travels down the groove to the bottom position where it remains for the rest of the run. The point at which the basket drops is recorded by a temporary drop in batch temperature.

Pre-activation of the catalyst, heatup, pressurization, and a period of thermal reaction are accomplished after sealing the reactor, but before contacting catalyst and slurry. The catalytic period starts when the basket is dropped into the liquid and stops when the heater is removed from the autoclave. Figure 3, a typical temperature history of a run, shows that this sequence results in a well defined reaction period. Figure 3 also shows the endotherm that always occurs during heatup as the coal undergoes thermal dissolution.

Product Analysis

Product analysis schemes are similar for the two vehicles except for the addition of a distillation step in the tetralin runs (Figure 4). The vehicle remained with the coal liquefaction products in the heavy oil runs. The techniques used to separate oil (pentane soluble),

asphaltenes (benzene soluble, pentane insoluble), and pre-asphaltenes (pyridine soluble, benzene insoluble) are well known.

Effluent gas was monitored by GC for 50 runs, enough to establish that there were no significant differences among catalysts in the gases formed, nor between catalysts and no catalyst. It was concluded that light hydrocarbons come from the coal (not the vehicle) at the test operating conditions, whether or not catalyst is present.

Samples of the separator condensate and the distillate obtained during product workup were analyzed by GC for the tetralin runs. Particular attention was paid to the relative amounts of decalin, tetralin, and naphthalene as indicators of hydrogenation activity.

The results are presented in terms of elemental analyses of product (%S, %N, and H/C atomic ratio); extraction analyses (oil/asphaltene ratio and % pre-asphaltenes); the decalin/naphthalene ratios of distillate and separator product (for tetralin runs); and conversion. Conversion is defined as 100 less the percent MAF coal charged that remains benzene insoluble. Note that the chemical analyses refer to coal plus vehicle in the heavy oil runs, but only to coal products in the tetralin runs.

Catalysts

Eight 1/8 in. tabletted catalysts were tested in the heavy oil series at 4000 psig. Four of these tablets and ten 1/16 in. extrudates have been tested to date in the runs with tetralin at 2500 psig. Various blank and duplicate runs were made with both vehicles.

The reference catalyst is Harshaw's CoMo-0402 T 1/8, which has been reported in connection with work on the Synthoil process and other studies. Other catalysts are designated either by their commercial name (as HT-400) or by a simple chemical notation (as NiMo). The catalysts tested to date represent a variety of chemical compositions and support structures. For example, two sets of NiMo extrudates were made to have systematically varying pore structure; these are designated on Table 2 as A-1, B-1, etc.

Catalysts are loaded on a volume basis (25 cc). Packed densities cover a wide range, tablets running 1.0 - 1.1 g/cc and extrudates 0.6 - 0.8 g/cc. Weight of catalyst charged therefore ranges from about 15 to 28 g.

General Results

Test results from runs with heavy oil vehicle are summarized in Table 1, and from tetralin runs in Table 2. All runs were at the operating conditions given above except for the few special run times indicated by notes to the tables. The runs are listed in order of decreasing oil/asphaltene ratio in the product.

Mass recoveries typically run 97 to 99% with heavy oil and higher with tetralin; the small variations do not affect the conclusions. "Conversion" of coal to liquids also falls within a narrow range for standard runs and does not differentiate among catalysts. Thermal conversion (no catalyst present) is about 2-3% lower than the average catalytic conversion with heavy oil, and about 6-7% lower with tetralin. The fact that the catalytic conversions are close attests to the reproducibility of the test, for conversion varied widely when time was varied as in Runs 18, 19, and 20. Excellent reproducibility

is also demonstrated by the similar results found in duplicate Runs 32 and 50, and 29 and 52 (Table 2).

As noted earlier, the amount and composition of effluent gases do not appear to be influenced by the presence of a catalyst. Similarly, the amount of separator condensate is essentially constant for a fixed run time. However, its composition is related to the activity of the catalyst used, as may be seen from the decalin/naphthalene ratios given in Table 2. The data show that separator product is more saturated than the solvent which remains in the reactor and becomes "distillate".

Special Runs

The marked effect of a catalyst on sulfur removal, H/C ratio, and conversion of asphaltenes to oils is seen from comparison of Run 9 (no catalyst) with any of the catalytic runs on Table 1. However, removal of nitrogen heteroatoms from the coal appears to be nearly as difficult with a catalyst as without.

Comparison of Runs 24 and 27 (Table 2) shows the effect of catalyst on tetralin in the absence of coal. Much more decalin was made in the presence of a catalyst: 1.4% in Run 24, but 48% in Run 27.

In three instances run time was varied with the same catalyst. Runs 19, 20, and 18, with the reference CoMo catalyst, had catalytic run times of 0.4, 2.0, and 2.5 hrs. Without exception, as run time increases, H/C and oil/asphaltene ratios increase and % pre-asphaltenes and % S decrease.

In the tetralin series, Run 43 had 0.5 hr more thermal exposure than Run 42, other things being equal, and showed more reaction in each of the variables tabulated. Similarly, Run 36 (1 hr thermal, 2 hr catalytic) shows more reaction than Run 35 (2 hr thermal, 1 hr catalytic) with the same catalyst.

Comparison of Catalysts

In general, the data indicate that all the measures of catalytic activity are interrelated. Inspection of Tables 1 and 2 shows that the following properties coincide:

- high oil/asphaltene and H/C ratios, both measuring the extent of hydrogen addition to the coal,
- low S and N in the product (the latter less definitely) and lower % pre-asphaltenes, all measures of catalytic action on the liquefied coal,
- high decalin/naphthalene ratio in both distillate and separator products, showing activity in solvent hydrogenation.

The correlation between H/C and oil/asphaltene ratios is shown graphically in Figures 5 and 6. With respect to the heavy oil runs (Fig. 5), all the points except Run 19 (0.4 hrs) appear to fit a correlation. It is concluded that some kind of thermalequilibrium between coal, solvent, and hydrogen has been reached in the standard length runs, and more hydrogen addition is achieved either by longer contact time or a better catalyst. The activity differences among catalysts in the heavy oil runs are relatively small in spite of the variety of compositions employed. It is believed that the uniformity of

results is due, in part, to the fact that the vehicle is not separated from the coal and plays a major role in the observed results. Another reason may be the use of tablets in this series. Tablets tend to have similar pore structures at their external surfaces which may mask chemical differences.

Table 2 and Figure 6 show a wider range of results with tetralin and extruded catalysts. Certain NiMo catalysts have demonstrated very good relative performance in this test. However, the six NiMo catalysts tested in Runs 37 - 43, differing primarily in pore structure, show little difference in performance. It is premature to draw firm conclusions regarding the key factors that affect catalyst activity, and more work is required before relating performance to properties.

NiW catalysts have not shown up well vs. NiMo in the few tests completed. Regarding CoMo, the best comparison so far between similar NiMo and CoMo catalysts is in Runs 32 and 50 vs. 33; the NiMo catalyst appears to be somewhat more active in each category. It is interesting, however, that the CoMo causes less saturation of the solvent than expected from its position on the table. The same thing may be said of the tableted version (Run 31). This may be an advantage.

The four tablets tested on tetralin gave similar results (Table 2). As expected, they are less active than corresponding 1/16 in. extrudates. The similarity of tablet results parallels the same finding on the heavy oil feed.

Principal Conclusions

Conversion of coal to benzene soluble liquids is primarily a thermal reaction dependent on temperature and time, only secondarily on catalyst. Addition of hydrogen to the coal liquids and solvent and removal of heteroatoms are greatly influenced by the catalyst, and these characteristics tend to correlate with each other. This suggests that one mechanism such as rehydrogenation of the solvent may be the dominating process which separates good from bad catalysts.

If this picture of the process is valid, the catalysts selected by this screening test are likely to be effective not only in direct liquefaction processes, but also in processes where catalytic upgrading of the coal liquids is separated from the liquefaction step.

Several catalysts have been identified which show better short-term performance than the reference CoMo tablet. The properties which lead to better catalyst performance have not yet been clarified, nor have aging tests been carried out.

The falling basket reactor solves a number of experimental problems in batch screening of catalysts for continuous processes, especially in separating thermal from catalytic effects and in providing a well defined reaction period. Reproducibility of results is excellent.

TABLE 1 RUNS WITH HEAVY OIL VEHICLE - RANKED BY OIL/ASPHALTENE RATIO

Run	Catalyst (1)	Conversion %	Pre-asphaltenes %	Benzene Solubles(2)		
				%S	%N	H/C(At.) Oil/Asphaltene
22 (3)	CoMo-0402	-	-	0.04	0.42	1.02
18 (4)	CoMo-0402	77.0	0.6	0.11	0.79	0.99
16	HT-400 CoMo/Al	75.6	0.2	0.18	0.81	0.96
21	CoMo-0402 + 0.1% Re	75.0	0.4	0.17	0.82	0.96
20	CoMo-0402	69.3	1.4	0.14	0.80	0.96
17	NiW/Al	74.1	0.8	0.10	0.94	0.94
12	NiMo/Si-Al	73.7	0.3	0.10	0.83	0.94
11 (6)	NiW/Al	74.7	0.2	0.11	0.95	0.98
15	CoMo/Al	75.1	0.6	0.14	0.79	0.95
14	CoMo/Al-Si	72.9	0.4	0.16	0.94	0.93
23	CoMo/SiMg-Al	65.6	1.0	0.23	1.01	0.90
19 (5)	CoMo-0402	52.9	2.1	0.30	1.00	0.83
9	No Catalyst	72.8	0.6	0.37	0.94	0.87

(1) All 1/8 in. tablets. Al = Al_2O_3 and Si = SiO_2

(2) Bz sols. = vehicle + liquefied coal.

(3) No coal.

(4) 2.5 hr. catalytic reaction time instead of 2.0 hr.

(5) 0.4 hr. catalytic reaction time.

(6) Carbonaceous material left in catalyst. Sample of same was used in Run 17 after complete calcination.

TABLE 2 RUNS WITH TETRALIN VEHICLE - RANKED BY OIL/ASPHALTENE RATIO

Run	Catalyst ⁽¹⁾	Conversion %	Pre-asphaltenes %	COAL LIQUEFACTION PRODUCT				decalin/naphthalene Separator Product	
				\$S	\$N	H/C (At.)	Oil/Asph.	Distillate	
32	HT-500 NiMo/Al E	77.9	0.0	0.02	0.96	1.10	2.6	2.7	-
34	HT-115 NiMo/Al E	79.4	0.1	0.06	1.04	1.07	2.3	1.6	3.0
50	HT-500 NiMo/Al E	77.8	0.2	0.02	0.02	1.06	2.1	2.7	5.6
37	NiMo/Al E A-1	78.6	0.1	0.05	1.15	1.06	1.9	1.6	2.1
43	NiMo/Al E B-2	78.8	0.0	0.02	1.19	1.08	1.9	1.6	2.1
33	HT-400 CoMo/Al E	75.7	0.0	0.04	1.19	1.05	1.8	0.8	1.3
38	NiMo/Al E B-1	78.1	0.2	0.06	1.05	1.05	1.8	1.7	2.0
40	NiMo/Al E B-3	78.0	0.0	0.02	1.08	1.08	1.7	1.4	1.8
41	NiMo/Al E A-2	78.9	0.0	0.05	1.05	1.05	1.7	2.0	2.2
42(2)	NiMo/Al E B-2	78.1	0.0	0.04	1.06	1.06	1.7	1.2	2.2
31	HT-400 CoMo/Al T	76.1	0.4	0.09	1.21	1.06	1.6	0.8	1.0
26	NiMo/Al T	77.5	0.3	0.07	1.10	1.05	1.5	2.1	2.9
30	NiW/Al T	73.6	0.5	0.12	1.28	1.04	1.4	0.9	1.4
39	NiMo/Al E A-3	78.6	0.1	0.04	1.04	1.04	1.3	0.7	2.0
29	CoMo-0402 T Ref.	78.0	0.2	0.09	1.24	1.03	1.1	0.8	1.3
52	CoMo-0402 T Ref.	77.7	0.3	0.10	1.01	1.01	1.1	0.9	1.7
36	NiW/Al E C-1	77.9	0.2	0.07	1.28	1.01	1.1	0.4	1.1
35(3)	NiW/Al E C-1	75.5	0.6	0.09	1.37	1.01	0.9	0.2	0.7
45	NiW/Al E C-2	74.6	0.9	0.18	1.01	1.01	0.8	0.8	1.4
28	No Catalyst	71.9	2.4	0.46	1.66	0.94	0.4	0.1	0.9
44	Alumina E	70.8	1.5	0.53	0.93	0.93	0.4	0.1	0.7
24(4)	No Catalyst	-	-	-	-	-	-	5.0	5.0
27(4)	CoMo-0402 T Ref.	-	-	-	-	-	-	206.0	12.3

(1) Al = Al₂O₃. E = 1/16 in. extrudate. T = 1/8 in. tablet.

(2) 0.5 hr. thermal reaction time instead of 1.0 hr. as in Run 43.

(3) 2.0 hr. thermal and 1.0 hr. catalytic instead of 1.0 and 2.0 as in Run 36.

(4) No coal.

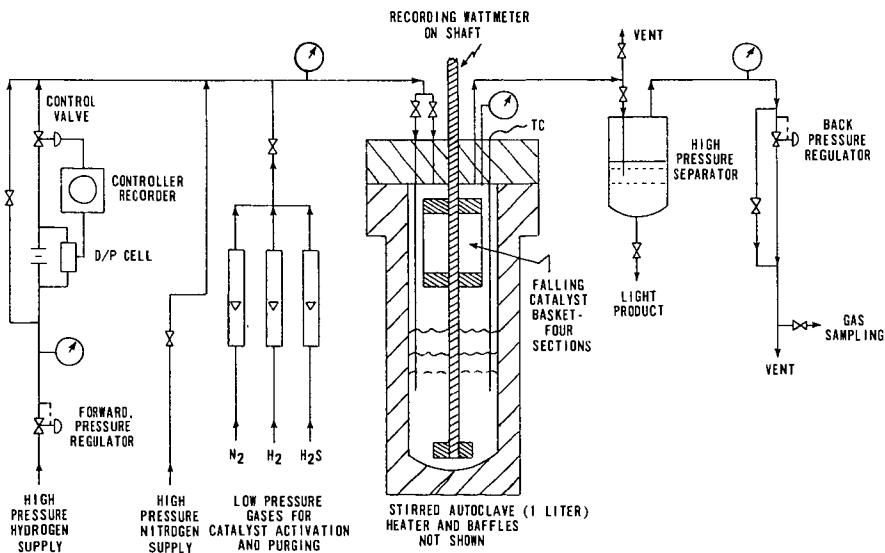
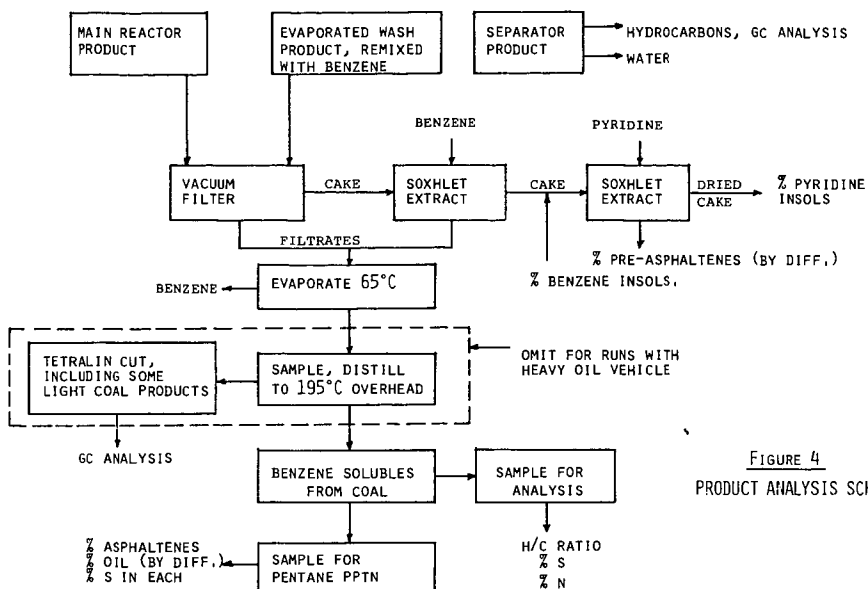


Figure 3
TEMPERATURE-TIME HISTORY
OF TYPICAL RUN
(HEAVY OIL VEHICLE)

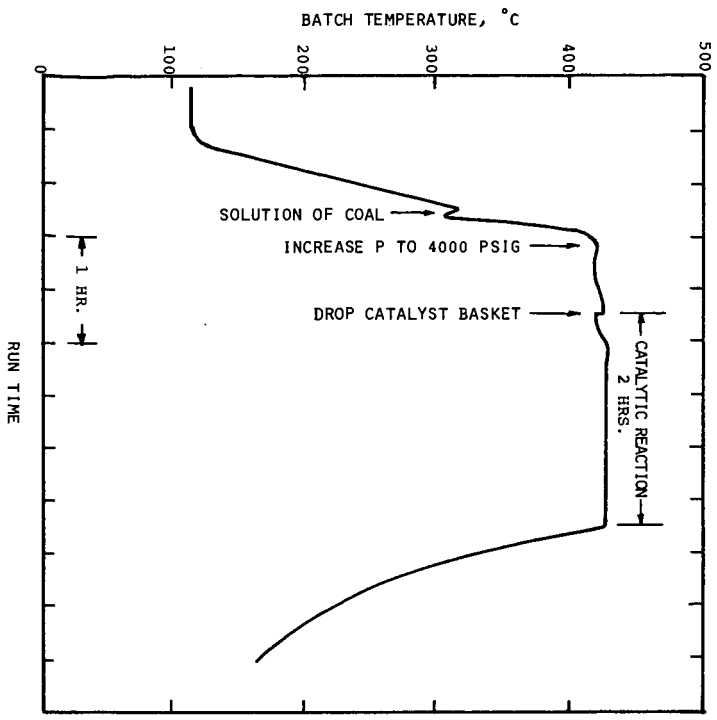
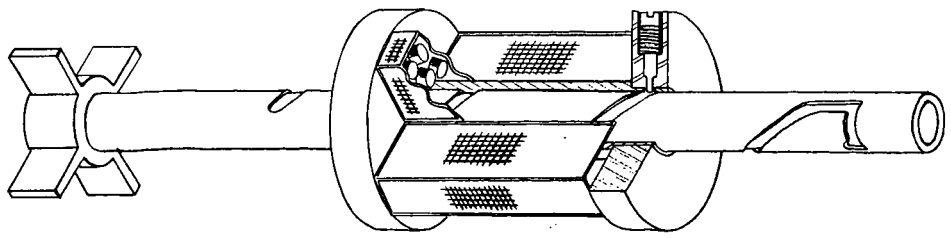
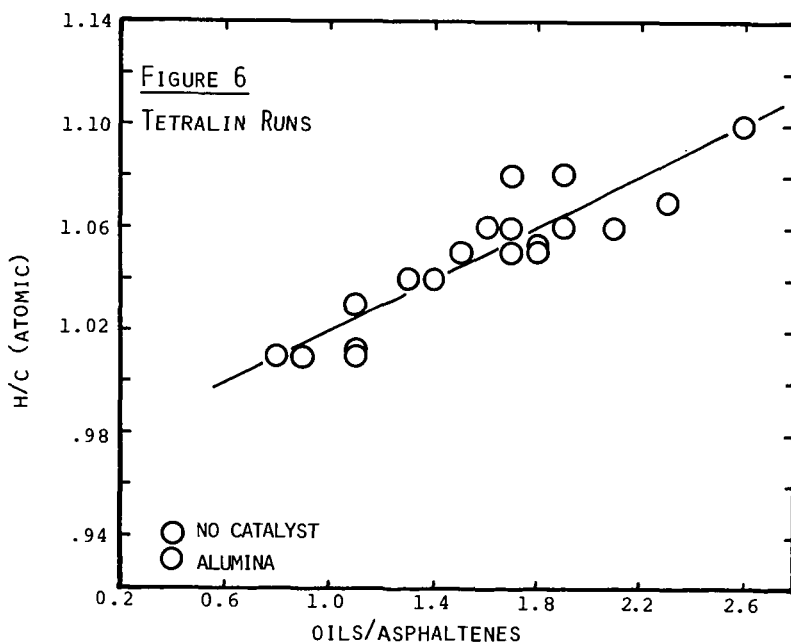
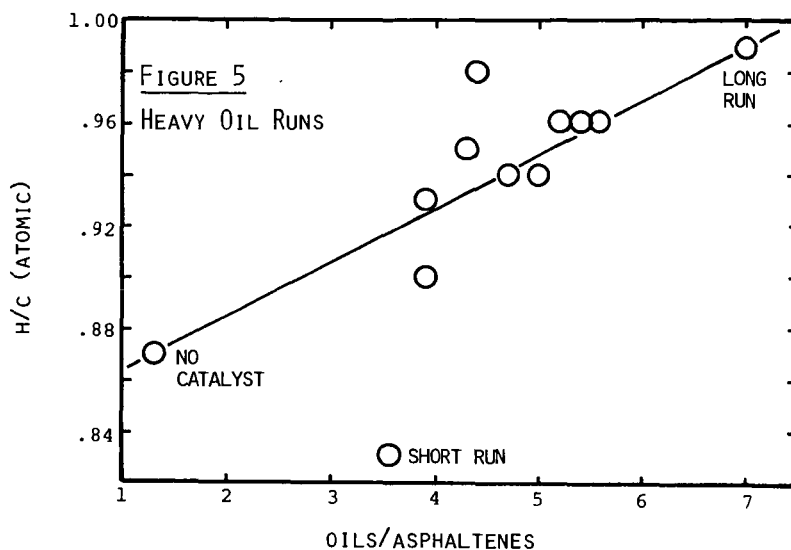


Figure 2
FALLING BASKET ASSEMBLY



CORRELATION OF H/C AND OIL/ASPHALTENE RATIOS IN LIQUEFACTION PRODUCTS



Catalyst Development for Hydroliquefaction of Coal¹

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Abstract

This paper summarizes observations made during the development of a catalyst screening test in the initial phases of a program which has as its objective the development of improved catalysts for the direct hydroliquefaction of coal.

The test is carried out batchwise in a stirred autoclave and employs Illinois #6 coal and a commercial petroleum based solvent (Panasol AN3). Uncertainties in reaction time and temperature are normally encountered in this mode of operation due to substantial coal conversions during heating and cooling. These uncertainties have been reduced significantly by injecting coal after a slurry of solvent and catalyst has reached operating temperature and by rapid cooling at the termination of the reaction period.

Products are separated into benzene insoluble, pentane insoluble (asphaltene) and pentane soluble (oil) fractions. Data obtained with a commercial CoMo catalyst in a study of the effect of reaction variables on hydrogen consumption, coal conversion, asphaltene and oil yields, and sulfur removal indicate the following:

Hydrogen absorption is linear with time and continues after maximum coal conversion (93%) is reached. It is also linear with pressure in the range investigated (760-3000 psi) indicating a process first order in hydrogen and therefore independent of coal conversion which becomes zero order in hydrogen above 2000 psi.

A clearcut distinction between first and zero order dependence on coal in the 50-80% conversion range cannot be made. The reaction tends toward first order at higher conversion levels. Substantial conversion of coal is observed in the absence of catalyst and at very short reaction times.

Asphaltene yields are proportional to conversion until about 80% conversion and remain relatively constant thereafter. Oil yields increase with conversion to maximum conversion (93%).

¹ ERDA Contract No. EF-76-C-01-2335

Sulfur levels in asphaltene and oil decline with increasing yields of these fractions.

The relationship between asphaltene and oil yields and sulfur contents is not affected by temperature or catalyst loading.

Most of these observations can be rationalized via a model in which the major role of catalyst is to maintain the solvent in a suitable state of hydrogenation. Moreover, the data support a branching mechanism for formation of asphaltenes and oil rather than the generally assumed sequence of first order reactions.

EFFECTS OF MINERAL MATTER ON THE HYDROLIQUEFACTION OF COAL

by

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INTRODUCTION

Several previously published studies have shown that the naturally occurring minerals in coal may play a significant role in hydroliquefaction (1-6). The extent of conversion was shown to correlate with total mineral content (1,2,4). Iron - in the form of pyrite, pyrrhotite and liquefaction residue - has been shown to affect conversion and hydrogenation (2-4). Coal ash, pyrrhotite and liquefaction residues have all exhibited some activity for the desulfurization of coal (2,5), and pyrrhotite has been shown to be more active than pyrite for the desulfurization of thiophene (5). Pyrite and several clays were shown to catalyze the isomerization of tetralin to methyl indane and the transfer of hydrogen from hydroaromatic to aromatic structures (6).

We have shown, for a series of high-volatile bituminous coals having similar maceral contents, that the extent of conversion, product viscosity and hydrogen consumption could be correlated with the mineral content (4). The combined role of pyrite, clays and organic sulfur was shown, but the independent effect of each of these components was not investigated in our previous work. To better understand the role of minerals in the hydroliquefaction of coal, we decided to carry out a number of experiments, in a stirred autoclave, in which pure minerals, liquefaction residues and a commercial catalyst were added to the feed coal. The experimental conditions (temperature, heating rate, pressure, residence time and solvent-to-coal ratio) were held constant for each run. Illinois No. 6 coal was selected for this work because of its moderate liquefaction reactivity (4). It was assumed that greater differences in conversion and product composition would be observed by augmenting the mineral content of a moderately reactive coal than by utilizing a very reactive (e.g., western Kentucky) coal.

EXPERIMENTAL PROCEDURES

The coal used in all of the experiments was Illinois No. 6 (Orient 4 Mine), which was pulverized to minus 100 mesh. Proximate, ultimate and sulfur forms analyses are given in Table 1. The mineral matter composition, also shown in Table 1, was obtained from the x-ray diffraction analysis of low temperature ash (7,8). The percentages of pyrite and mixed layer clays were approximately

one-half the corresponding values that were reported for the more reactive Kentucky No. 11 (Fies Mine) coal (4).

The solvent used was creosote oil, No. 4 cut, which was obtained from the Reilly Tar & Chemical Co. This oil had a specific gravity of 1.12 and a boiling range of 270-400°C. The solvent-to-coal (daf) ratio used in all runs was 2.50.

The minerals, catalyst and residue used for the spiking experiments are described in Table 2. Pyrite, pyrrhotite (FeS), clay and the liquefaction residue were included in this study because of their potential catalytic importance (1-6). Zinc sulfide was included because several Illinois coals have been found to have extremely high zinc contents (8). The zinc presumably occurred in the form of the mineral sphalerite (zinc sulfide). The commercial Co/Mo hydrodesulfurization catalyst was included as a reference "standard" with which to compare the activity of the other added species. The minerals were blended with the dry coal by milling in a mortar and pestle for a minimum of 15 min. In each of the spiking experiments, 2.50 g of the mineral, residue or catalyst was used; this was equivalent to 5% of the daf coal charge.

All of the liquefaction runs were carried out in a one-liter, stirred autoclave. The reactants were placed in a stainless-steel liner that had a volume of 0.7 liter. Nominal reaction conditions were:

Initial (cold) pressure	: 1000 psig hydrogen
Heatup time	: 1.0 hr
Temperature	: 405°C
Residence time at temperature	: 0.5 hr
Cooldown time	: overnight (18 hr)

At the end of each run, following cooldown, the overhead gases were vented through caustic scrubbers, and the liquid product was removed. Material accountability was routinely 95% or better. Solids separation was effected by centrifugation at 2200 rpm for 45 min. Product analysis included viscosity (Brookfield), elemental composition and Soxhlet solvent extraction. Conversion was calculated on the basis of both pyridine and benzene insolubles. The former was calculated from a forced ash balance (9), the latter was obtained from the expression:

$$\text{Percent conversion} = 100 \left[1 - (\text{OBI}_f / \text{OBI}_i) \right]$$

where OBI_f and OBI_i are the weight fractions of organic benzene insolubles in the final liquid product and initial reactants, respectively.

A crude estimate of hydrogen consumption was made by calculating the difference between the initial pressure (1000 psig in all cases) and the final pressure after cooldown. The pressure difference, ΔP , was normalized to that of the experiment in which no mineral or catalytic agent was added. A pressure ratio was then defined as:

$$\text{Pressure ratio} = \Delta P / \Delta P_0$$

where ΔP_0 was the pressure difference for the control (no added minerals) run. As defined above, the greater the pressure ratio, the greater was the hydrogen consumption. The formation of hydrocarbon gases could have had an effect on the ratio, but it was assumed that this would not alter the observed trends.

RESULTS AND DISCUSSION

Data from the autoclave experiments are given in Table 3. It has been shown in the literature that coal can be converted to greater than 90% pyridine solubles in less than three minutes under the proper reaction conditions (9,10). In the present case of relatively long heatup and residence times, reaction temperatures in excess of 400°C and use of a good liquefaction solvent, it is clear that transformation to pyridine solubles reached a plateau (92 to 94% conversion) that was independent of any added species.

The conversion of the initially solubilized coal to molecular constituents that are soluble in benzene is a slower process (9). This, in part, may be seen by the lower conversions to benzene solubles as shown in Table 3. Whereas the addition of mineral matter did not affect the conversion to pyridine solubles, certain species such as FeS, liquefaction residue and Co/Mo did have an effect upon the conversion to benzene solubles. It is of some interest to note that pyrite did not affect conversion, but pyrrhotite - both as FeS and as the predominant form of iron in the liquefaction residue (3,6,11) - did result in an increase in conversion. The Co/Mo catalyst had the greatest positive effect on conversion, and ZnS seemed to have a slightly negative effect as seen by the decrease in conversion.

Significant decreases in the viscosity of the liquid products were observed for the runs in which pyrite, pyrrhotite (FeS) and Co/Mo had been added. A smaller decrease in viscosity, which is probably not statistically significant, was noted when the liquefaction residue had been used. In the experiment with kaolinite, the viscosity of the product increased. This increase could have been caused by suspended particulate matter that was not removed by centrifugation. Zinc sulfide did not have any effect on product viscosity.

We have previously shown, for West Virginia coal, that the viscosity of a coal-derived liquid was dependent upon the organic benzene insolubles and asphaltene content, but the benzene insolubles had a significantly greater effect on viscosity than did asphaltene (4,12). The largest decrease in viscosity in the spiking experiments (Table 3) was observed when Co/Mo had been added to the feed. In this case, the asphaltene content of the resulting liquid product was essentially the same as that obtained in the control experiment, in

which no mineral or catalyst had been added. The addition of Co/Mo, however, resulted in a significant reduction in organic benzene insolubles, and the large decrease in viscosity was probably a direct consequence of this. The addition of pyrite resulted in the largest decrease in asphaltene content in the entire test series, but did not affect the benzene insolubles. The addition of pyrrhotite (FeS and residue) resulted in decreases in both the asphaltenes and organic benzene insolubles. The observed decreases in viscosity in these cases were attributed to corresponding shifts in the relative quantities of the asphaltenes and benzene insolubles. An interesting selectivity has been observed in which pyrite significantly affected only the asphaltene content, whereas pyrrhotite affected both the organic benzene insolubles and asphaltenes.

The hydrogen-to-carbon ratios of the centrifuged liquid products were quite similar (Table 3). The present data show that hydrogen consumption, as indicated by changes in the pressure ratio, increased in all of the spiking experiments. This increase was particularly significant in the run with Co/Mo, in which the pressure ratio increased almost three-fold. Since the H/C ratios of the liquid products were similar, it is proposed that hydrogen was primarily consumed for heteroatom removal, conversion of (initially solubilized) coal to benzene solubles and production of hydrocarbon gases. In the case of Co/Mo, the high hydrogen consumption, without a concomitant increase in the hydrogen content of the liquid product, would appear to be undesirable with respect to process economics.

Significant decreases in the sulfur content of the liquid products were found in the runs with FeS, ZnS and Co/Mo. In the experiment with pyrite, the sulfur content of the product was higher than the corresponding product from the control run where no minerals or catalysts had been added. This may have been due to the presence of extremely fine particles of inorganic sulfur that could not be removed by centrifugation. On the other hand, this could have been a consequence of the fact that pyrite is not an effective desulfurization catalyst. Work at Auburn University has shown that pyrite was less effective than no catalyst at all for the desulfurization of creosote oil (2). We have shown that pyrrhotite, FeS, was considerably more active for sulfur removal than either pyrite or the liquefaction residue (Table 3). This is in good agreement with the Auburn work (2), and with the data from a recent pulse microreactor study, where it was demonstrated that pyrrhotite was approximately four times more active than pyrite for the hydrosulfurization of thiophene (5). It is conceivable, therefore, that the non-stoichiometric iron sulfides, which are formed from the pyrite during coal hydroliquefaction (6,11), are the active species for desulfurization.

SUMMARY

Batch autoclave experiments have been carried out with Illinois No. 6 coal (Orient 4 Mine) in creosote oil. Various minerals, a dry liquefaction residue and a Co/Mo catalyst were added to the feed coal, while all process parameters (pressure, temperature, residence time, heating rate and solvent-to-coal ratio) were held constant. Significant increases in conversion to benzene solubles were observed when pyrrhotite (FeS), residue and Co/Mo had been used. Decreases in the viscosity of the liquid products were found in the spiking runs with pyrite, pyrrhotite and Co/Mo. The largest decrease in viscosity occurred in the experiment with Co/Mo and, in this case, a concomitant decrease in the organic

benzene insolubles was found. A selectivity was observed in which pyrite affected only the asphaltene content of the liquid product, but pyrrhotite affected both the asphaltenes and the organic benzene insolubles. The data have shown that pyrrhotite and Co/Mo were active for desulfurization, but pyrite and most of the other minerals were not. Hydrogen consumption, as estimated from differences in the venting pressure, increased in all spiking experiments - especially when Co/Mo had been added to the feed. The H/C ratios of the liquid products, however, were similar. This would imply that hydrogen had been utilized primarily for heteroatom removal, conversion to benzene solubles and hydrocarbon gas formation.

REFERENCES

1. D. K. Mukherjee and P. B. Chowdhury, Fuel 55, 4 (1976).
2. A. R. Tarrer, J. A. Guin, W. S. Pitts, J. P. Henley, J. W. Prather and G. A. Styles, Preprints, Div. of Fuel Chemistry, Amer. Chem. Soc., 21 (5), 59 (1976).
3. C. H. Wright and D. E. Severson, *ibid.*, 16 (2), 68 (1972).
4. B. Granoff and M. G. Thomas, *ibid.*, 22 (6), 183 (1977).
5. C. E. Hamrin, Jr., "Catalytic Activity of Coal Mineral Matter," Interim Report for the Period April-September 1976, FE-2233-2, February 1977.
6. P. H. Given, "The Dependence of Coal Liquefaction Behavior on Coal Characteristics," presented at the Short Course on Coal, The Pennsylvania State University, June 1976.
7. F. W. Frazer and C. B. Belcher, Fuel 52, 41 (1973).
8. C. P. Rao and H. J. Gluskoter, "Occurrence and Distribution of Minerals in Illinois Coals," Illinois State Geological Survey, Circular 476 (1973).
9. R. C. Neavel, Fuel 55, 237 (1976).
10. D. D. Whitehurst, M. Farcasiu and T. O. Mitchell, "The Nature and Origin of Asphaltene in Processed Coals," EPRI AF-252, February 1976.
11. J. T. Richardson, Fuel 51, 150 (1972).
12. M. G. Thomas and B. Granoff, Fuel (accepted for publication).

Table 1. Analysis of Illinois No. 6 Coal^a

<u>Proximate Analysis</u>		<u>Sulfur Forms</u>	
Volatile Matter	36.69	Pyritic	1.27
Fixed Carbon	52.60	Sulfate	0.09
Ash	10.71	Organic	1.64
<u>Ultimate Analysis</u>		<u>Mineral Matter</u>	
Carbon	71.48	Pyrite	2.80
Hydrogen	4.89	Quartz	2.20
Nitrogen	1.45	Calcite	0.78
Sulfur	3.00	Kaolinite	0.82
Oxygen (difference)	8.47	Mixed Clays	6.35
Ash	10.71		

^a All data given as a percent of the coal on a dry basis.

Table 2. Minerals and Catalysts Used for the Spiking Experiments

<u>Mineral</u>	<u>Description</u>
FeS ₂	Single crystal pyrite from Sinaloa, Mexico. Pulverized to minus 200 mesh.
FeS	Obtained from Cerac/Pure, Inc. as minus 100 mesh powder. Identified as pyrrhotite, Fe _{1-x} S, by x-ray diffraction (x = 0.14).
ZnS	Obtained from Cerac/Pure, Inc. as minus 325 mesh powder.
Kaolinite	Obtained from a clay deposit in Lewiston, Montana. Pulverized to minus 100 mesh.
Co/Mo	Commercial hydrodesulfurization catalyst (Harshaw O402T). Crushed and screened to 45 x 100 mesh.
Residue	Acetone-washed filter cake obtained from previous run with Illinois No. 6 coal in creosote oil. Used in the form of a dry, minus 100 mesh powder. (Ash = 48.4%; sulfur = 4.9%).

Table 3. Data from the Autoclave Experiments

	None	Added Minerals or Catalyst					Residue	Co/Mo
		Pyrite	FeS	ZnS	Kaolinite			
Conversion (% daf)								
Pyridine Solubles	93	94	93	93	92		92	93
Benzene Solubles	38	38	46	34	38		44	63
Viscosity ^a (cps @ 60°C)	355	271	290	351	418		338	112
Solvent Analysis (% daf)								
Organic Benzene Insols.	17.7	17.6	15.4	18.9	17.8		16.1	10.4
Asphaltenes	19.6	15.3	16.8	16.2	19.6		18.9	19.8
Pentane-soluble Oils	62.7	67.1	67.8	64.9	62.6		65.0	69.8
Elemental Analysis ^a (% daf)								
Carbon	87.93	88.04	88.02	88.09	87.40		87.99	87.95
Hydrogen	5.84	6.00	5.92	5.92	5.83		5.89	6.02
Nitrogen	1.34	1.32	1.38	1.30	1.37		1.25	1.23
Sulfur	0.75	0.86	0.57	0.67	0.73		0.72	0.49
Oxygen (difference)	4.14	3.78	4.11	4.03	4.67		4.15	4.31
H/C	0.80	0.82	0.81	0.81	0.80		0.80	0.82
Pressure Ratio ^b	1.0	1.3	1.2	1.1	1.1		1.3	2.9

^aCentrifuged liquid product.

^b $\Delta P/\Delta P_0$ as defined in text.

EVALUATION OF USE OF SYNGAS FOR COAL LIQUEFACTION

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INTRODUCTION

With the feasibility of coal liquefaction having been demonstrated over forty years ago, the major emphasis since then has been on process modifications and catalyst development to improve the process economics [1]. Cost analysis of a typical coal liquefaction process [2] reveals that as much as 30 percent of the overall cost is related to hydrogen production. The proposed modification is to use syngas ($H_2 + CO$) and steam instead of H_2 as feed gas to the reactor. The advantages of this modification are presented.

The bench scale approach in the direct liquefaction of coal consists of treating a slurry of coal in solvent under high H_2 pressure at temperatures of 400-475° C. The large coal molecules fragment thermally and are hydrogenated via hydrogen transfer from a donor solvent. The liquid product is formed as the H/C atomic ratio of coal increases from 0.7 to an approximate value of 0.9-1.0. Lighter liquid products could be formed with additional H_2 uptake. A catalyst would serve to promote hydrogenation and desulfurization processes during liquefaction. The required H_2 , usually 3-6 weight percent of the coal feed, is produced by gasification of coal and residual char to produce a synthesis gas. The synthesis gas as produced is a mixture of H_2 , CO, H_2O , and some CO_2 . The "raw" syngas is then passed through a shift converter to produce CO_2 and additional H_2 . Since the gas still contains about 2-3 percent residual CO, further processing will be required before the gas can be used with a CO-sensitive catalyst [3].

SYNTHESIS GAS CONCEPT

The syngas approach is to bypass the expensive gas purification and shift conversion step and send the product from the gasifier directly to the liquefaction reactor along with the recycle gas and added steam. The CO in the feed gas reacts with steam to form H_2 ($CO + H_2O \rightarrow H_2 + CO_2$) in the liquefaction reactor rather than separately in the water-gas shift system. This can be accomplished by utilizing a bifunctional catalyst in the liquefaction reactor, consisting of the conventional CoMo-SiO₂-Al₂O₃ for liquefaction and desulfurization, which is impregnated with K₂CO₃ to catalyze^{2,3} the shift reaction.

The obvious advantage of this modification is the elimination of the capital and operating cost of the purification and shift steps. In addition there will be a slight improvement in the thermal efficiency of the process. There is a need, however, for a larger recycle gas cleanup step capable of removing both H_2S and CO_2 . Before the process can be considered viable it must be proven that the liquefaction activity in the presence of CO, H_2 and H_2O is comparable to that with H_2 .

To evaluate the effect of substituting synthesis gas for H_2 , we decided at first to look at the SYNTHOIL process. The experimental section explains how the direct catalytic coal liquefaction performance using H_2 and H_2 -CO was compared in a set of autoclave experiments. The results of a batch reactor cannot be simply used to predict the steady state conditions in a continuous commercial reactor. An attempt was made, however, to calculate flow conditions for coal liquefaction processes using H_2 and H_2 -CO on the same basis using autoclave data. The objective is a preliminary study to evaluate and compare the potential merit of using syngas rather than to calculate the accurate results for a commercial process. The evaluation of SYNTHOIL by Kattel [2] was used as the basis for the conceptual design.

EXPERIMENTAL AND RESULTS

The concept of liquefying coal with syngas was tested in a stirred autoclave. The autoclave was charged with 30 grams of West Virginia bituminous coal, 70 grams of Solvent Refined Coal process solvent, 10 grams of H_2O , and 2-3 grams of crushed CoMo- K_2CO_3 catalyst. The autoclave was then charged with a 2:1 H_2 -CO gas mixture to 1500 psi (gage), heated to 450° C (operating pressure 2800-3000 psi), held at 450° C for 15 min. and then rapidly cooled by running water through an immersed cooling coil.

The CoMo- K_2CO_3 catalysts were prepared in three ways: (1) by blending ground CoMo-SiO₂-Al₂O₃ catalyst (Harshaw 0402T) with K_2CO_3 powder, (2) by impregnating the CoMo catalyst with aqueous carbonate solution, (3) by introducing K_2CO_3 early in the preparation of CoMo catalyst in place of silicated alumina and keeping the ratios of Co and Mo to alumina constant. We have also tested CoMo catalysts impregnated with sodium carbonate, potassium acetate and barium acetate, NiMo catalyst impregnated with K_2CO_3 , and NH_4Mo catalyst. Some results have been presented previously [2]. Table I shows some representative results as well as hydrotreating data obtained with pure H_2 and CoMo-SiO₂-Al₂O₃ catalyst. The performances with H_2 -CO and H_2 compare very closely in all categories.

PROCESS EVALUATION

Using the yields obtained from the autoclave experiments and the process parameters of the SYNTHOIL process, material balances were derived for both the H_2 -CO and H_2 systems. An energy balance was then calculated for the H_2 -CO process scheme. Finally an economic comparison of the two alternatives was performed, based on an economic evaluation of the SYNTHOIL process made by Kattel, et al [2]. The benefit of using a high pressure gasifier (such as in the Texaco process) and a modification of the Exxon Donor Solvent Process using syngas were also examined.

A. Direct Catalytic Liquefaction of Coal

The flowsheet for the modified direct catalytic liquefaction process is shown in Figure 1. Synthesis gas from the gasifier is sent directly to the liquefaction reactor eliminating the shift and purification steps. Steam is added to the liquefaction reactor to promote the water-gas shift reaction. Now that this reaction is taking place in the liquefaction reactor, the CO_2 produced there must be removed in the recycle gas cleanup step. Therefore, the recycle gas cleanup step must be designed to remove both CO_2 and H_2S . It is desirable to produce a concentrated stream of H_2S to allow efficient use of the Claus process for converting H_2S to sulfur. The concept employed in the Giammarco-Vetrocoke process [5] for acid-gas removal meets these requirements. It will remove both CO_2 and H_2S from a gas stream and process it into two separate streams of CO_2 and H_2S .

The aqueous stream from the vapor-liquid separators is sent to an ammonium sulfate and sulfuric acid recovery process. The product slurry from the high temperature separator is centrifuged. The underflow from the centrifuge is sent to a char de-oiling process for recovery of oil entrained in the solids. Unconverted char from this step is sent to the gasifier for further carbon utilization.

TABLE 1. Hydrotreating of Bituminous Coal^a

(Coal: SRC Liquid = 1:2.3, 3000 psi, 450° C, 15 min)

Catalyst	Syngas (H ₂ :CO = 2:1)						H ₂	
	CoMo-K ₂ CO ₃ ^b	CoMo-K ₂ CO ₃ ^b	CoMo-K ₂ CO ₃ ^c	CoMo-BaAc ^b	NiMo-K ₂ CO ₃ ^b	NH ₄ Mo ^b	CoMo ^d	CoMo ^e NH ₄ Mo
% K ₂ CO ₃	11.2	5.0	7.7	(9.9) ^f	10.1	-	-	-
Surf. Area m ² /g	74	133	136	141	140	-	123	153
Conversion, %	94	90	90	89	89	90	94	91
Oil yield, %	68	60	63	61	59	57	71	62
Asphaltene formed, %	42	42	32	24	32	19	30	25
S in oil product, %	0.40	0.44	0.41	0.41	0.40	0.37	0.39	0.33
Kinematic viscosity, CS* at 60° C	20	18	18	16	21	13	15	13
Syngas or H ₂ consumed, SCF/lb maf coal	8.6	9.9	10.0	10.0	9.0	11.2	10.7	11.6
								10.2

^aData are given in weight percent of maf coal^bCoMo or NiMo impregnated with K₂CO₃ solution^cLaboratory prepared sample with K₂CO₃ substituted for alumina^dHarshaw 0402^eLaboratory prepared sample with the same composition as Harshaw 0402^fPercent barium acetate

Mass Balance - The basis of the flowsheet calculation is briefly described in the Appendix. There are two major problems associated with the batch autoclave data: (1) the solvent is not a recycle solvent derived at the identical steady state condition, and (2) the material balance is usually poor with a recovery in the range of 94-98%. Batch data from the autoclave experiments were used in the calculation as shown in the Appendix. The conversion of CO is calculated by assuming water-gas shift equilibrium at 475° C (28° C approach) with a H_2 :CO: H_2O feed of 2:1:0.4. The resulting yields for a continuous reaction are shown in Table 2. The flowsheet derived from these yields is shown in Figure 1.

The overall mass balances for the H_2 -CO and H_2 processes were obtained on the basis of one ton of West Virginia bituminous coal feed (See Table 3). The mass balance over the reactor, which operates at 4000 psig and 450° C, is based on the simulated yields. The design parameters used in the study are listed in the Appendix. It was assumed that the recycle gas scrubber provided complete removal of CO_2 and H_2S . The flow and composition of the off-gas from the vapor-liquid separators were estimated from vapor-liquid equilibria of the various components with the liquid oil at the separator temperatures of 150 and 40° C. The gasifier mass balance was based on the total gas demand, coal and char feed, operating condition of 450 psi and 982° C, 95% carbon conversion and a water-gas shift equilibrium at 1010° C (28° C approach).

Energy Balance - The thermal efficiency of the SYNTHOIL Process has been estimated by Akhtar et al [6]. The energy balance for the H_2 -CO process was computed and is shown in Figure 2. It is based on the net heats of combustion at the specified temperature of each stream, neglecting pressure effects. The net heats of combustion of the coal (12,390 Btu/lb), oil (16,300 Btu/lb), and the char (4,500 Btu/lb) were obtained experimentally. The heat capacities for coal, char, ash and oil were obtained from IGT's Coal Conversion Data Book. The energy balance across the reactor was calculated using eqn. 6 in the Appendix, assuming an adiabatic reaction with an estimated heat loss. The conceptualized plant is totally self-sufficient with the coal being the only energy input. The plant contains its own steam and electricity plant. The overall thermal efficiency is 75.6 percent as compared to values of 67.8 [2] and 74.9 [6] percent for the SYNTHOIL process using H_2 . The advantage of the syngas system is a result of the elimination of the inefficient two-stage shift reactors.

Economics - The methods used to perform the economic analysis of the two alternative cases followed those used in Katell's report. The main objective of this economic evaluation is to obtain a relative cost comparison of the two processes rather than to yield accurate estimates. The sequence of steps in the evaluation was as follows: (1) size major equipment, (2) cost major equipment, (3) use standard factors to cost miscellaneous equipment, (4) calculate utility balance, (5) size and cost utility sections, (6) determine operating costs and (7) do a discounted cash flow analysis over the life of the plant to determine the product selling price at various rates of return and coal prices. The analysis was carried out for both the CO - H_2 and H_2 cases. A unit cost table, which shows the cost distribution among the various sections of the process, is shown in Table 4. Two major differences are apparent in the unit cost table. The recycle gas cleanup and byproduct recovery sections in the H_2 -CO process are more expensive than that in the H_2 process because of the necessity of removing CO_2 in addition to H_2S in this stage. The cost of the shift and purification section is \$1.90/bbl in the H_2 process, but is totally absent in the H_2 -CO system. Thus the H_2 -CO system results in a net cost advantage of \$1.59/bbl or about 14% of the total process cost.

TABLE 2. Product Yields and Analysis at Steady State
(Basis 100 lb of maf coal feed)

Input		Syngas	H ₂
maf coal		100.00	100.00
H ₂		1.17	3.79
CO		35.20	0.00
H ₂ O		<u>25.81</u>	<u>0.00</u>
Total		162.18	103.79
H ₂ or H ₂ + CO consumption, SCF		661	675
Output			
C ₁ -C ₄		11.37	10.80
Oil		77.38	77.87
H ₂ O		9.08	5.99
CO ₂		55.31	0.00
H ₂ S		2.54	2.54
NH ₃		0.50	0.59
Char		<u>6.00</u>	<u>6.00</u>
		162.18	103.79
Elemental	Coal	Product Oil	Product Oil
C	73.8	88.3	88.3
H	5.2	7.5	7.7
O	7.2	2.6	2.5
N	1.3	1.2	1.1
S	3.8	0.4	0.4
Ash	8.2	-	-
Moisture	0.5	-	-

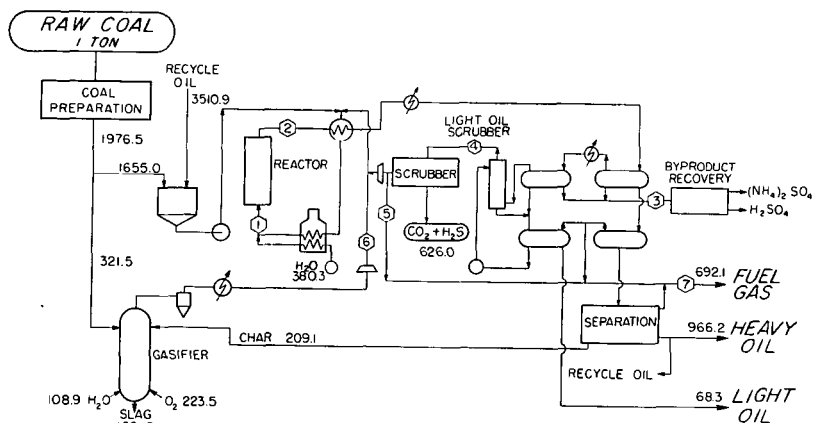


Figure 1-Process flow diagram using SYNGAS.

STREAM COMPOSITION

STREAM	①		②		③		④		⑤		⑥		⑦	
COMPONENT	lbs	(vol %)	lbs	(vol %)	lbs	(vol %)	lbs	(vol %)	lbs	(vol %)	lbs	(vol %)	lbs	(vol %)
MAF COAL	1511.4		0											
ASH	160.0		160.0											
CHAR	16.6		107.3											
OIL	3478.2		4647.8				26.1		0.2				144.8	
GAS COMPOSITION														
H ₂ O	390.0	(9.50)	137.2	(3.58)	137.2						1.4	(0.22)		
H ₂	239.3	(52.08)	221.5	(51.65)			217.0	(57.16)	4.3	(57.83)	26.6	(36.37)	11.5	(26.37)
CO	1628.1	(25.50)	1096.1	(18.40)			1052.8	(19.96)	21.1	(20.19)	596.4	(58.67)	643	(10.60)
Cl	391.9	(10.72)	452.4	(13.26)			399.8	(13.23)	8.0	(13.39)			65.0	(18.71)
C ₂	72.2	(1.06)	111.5	(1.75)			73.6	(1.31)	1.5	(1.32)			39.3	(6.06)
C ₃	33.8	(0.34)	81.2	(0.88)			34.5	(0.42)	0.7	(0.43)			47.4	(5.03)
C ₄	5.7	(0.04)	30.2	(0.24)			5.8	(0.05)	0.1	(0.05)			24.5	(1.94)
H ₂ S	36.3	(0.47)	74.8	(1.03)	15.1		179	(0.53)	0		36.3	(2.94)	41.8	(4.38)
CO ₂	202	(0.20)	856.1	(9.15)			608.1	(7.34)	0		20.2	(1.26)	247.9	(26.00)
NH ₃	0	(0)	76	(0.21)	76									
N ₂	5.5	(0.09)	5.5	(0.09)							5.5	(0.54)	5.5	(0.90)
Total....	7989.2	(100)	7989.2	(100)	1599		2435.6	(100)	35.9	(100)	686.4	(100)	692.0	(100)
scf....		81820		76350				67610		330		13030		7780

TABLE-3 OVERALL MASS BALANCE

In:	H ₂	H ₂ /CO
Raw Coal	2000.0	2000.0
Gasifier Steam Feed	141.4	108.9
Gasifier O ₂ Feed	187.0	223.5
Shift Converter Steam	558.2	0
Reactor Water Feed	0	380.3
Total	2886.6	2712.7
Out:		
Water Condensate	249.1	30.4
Waste Water	118.9	159.9
Slog	169.6	169.8
Fuel Gas	365.0	692.1
H ₂ S + CO ₂	946.4	626.0
Oil Product	1037.6	1034.5
Total	2886.6	2712.7

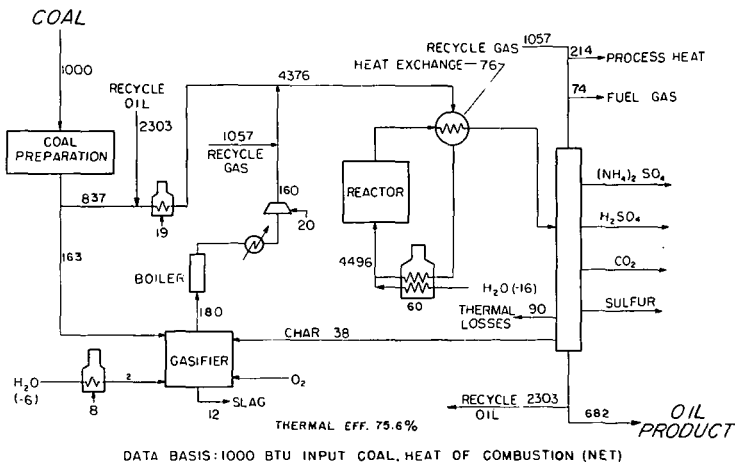


Figure 2-Thermal balance.

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TABLE 4. Unit Cost, \$/bbl Product Oil

<u>Cost</u>	<u>Operating</u>	<u>Capital</u>	<u>Credits</u>	<u>Total</u>
Coal + Paste Preparation	0.899	0.670	0	1.569
Hydrogenation	2.102	2.180	-2.366	1.916
Heat Exchange	0.666	1.178	0	1.844
Char De-oiling	.205	.362	-0.315	.252
Gasification	1.985	.174	0	2.159
Gas Cleanup + Byproduct Recovery	.819	.837	-.105	1.551
	<u>.593</u>	<u>.750</u>	<u>-.105</u>	<u>1.238</u>
Shift + Purification	0	0	0	0
	<u>1.206</u>	<u>.694</u>	<u>0</u>	<u>1.900</u>
Flue Gas Processing	.431	.431	-.232	0.630
Total	7.107	5.832	-3.018	
	<u>8.087</u>	<u>7.439</u>	<u>-3.018</u>	9.921
		Processing Cost		<u>11.508</u>
Underline - Cost using H ₂ Otherwise both H ₂ and H ₂ -CO systems have the same cost.		Coal Cost		9.453
		Oil Cost		19.374
				<u>20.961</u>

Basis: 25,000 BBL/D
 Cost based on April 1977 CE index
 WVa Coal - \$25/T
 15% return on investment

High Pressure Gasifier - A beneficial modification to the H_2 -CO process is to employ a high pressure gasifier to be operated at a pressure in the range of 2500-3000 psi, equivalent to that required in a liquefaction reactor. This change would further increase the thermal efficiency and improve the economics. From the energy balance (Figure 2) we see that 2% of the input energy exists as latent heat in the hot gasifier output. Also 2% of the input energy is used to compress the gasifier product gas. By employing a high pressure gasifier all of the latent heat is recovered, the inefficient gasifier heat exchanger is eliminated, the make-up gas compressor is not required and the reactor preheat duty is reduced. Thus the use of higher pressure gasifier increases thermal efficiency by about 4 percent. A minor offsetting change is the increased pressure of O_2 and steam necessary to feed the gasifier.

B. Extractive Hydrogenation of Coal

Coal liquefaction processes by extractive hydrogenation such as the Exxon Donor Solvent Process can also be benefited economically by using syngas in place of H_2 . A conceptual process scheme is presented in Figure 3. Coal is dissolved in a recycling solvent in the absence of catalyst under H_2 -CO pressure, and part of the liquid product is subsequently hydrotreated with syngas and steam in the presence of CoMo- K_2CO_3 catalyst to make the recycle solvent. Experimental data were obtained by initially hydrotreating an SRC solvent with syngas and steam in the presence of CoMo- K_2CO_3 catalyst and subsequently using this hydrotreated solvent to extract coal in the absence of catalyst. Table 5 shows the autoclave experimental results of hydrotreating the SRC solvent with syngas and H_2 . Table 6 shows the comparison of using the syngas hydrotreated solvent and the H_2 hydrotreated solvent for coal solvolysis under H_2 -CO and H_2 pressures respectively. From both tables, no significant difference in the quality of the product oil or solvent was observed between the syngas and H_2 systems.

REFERENCES

1. Bergius, F., German Patent 303272 (1922).
2. Kattel, S., "SYNTHOIL Process-Liquid Fuel from Coal Plant," Report No. 75-20, Bu. of Mines, Morgantown, WVa., Jan. 1975.
3. Vernon, L. W., Pennington, R. E., U.S. Patent 3,719,588 (1973).
4. Fu, Y. C., Illig, E. G., Ind. Eng. Chem., Proc. Des. Dev., Vol. 15, No. 3, 392, 1976.
5. Riesenfeld, F. C., Mullowney, J. F., Oil and Gas J., Vol. 57, No. 20, 86, 1959.
6. Akhtar, S., Lacey, J. J., Weintraub, M., Reznik, A. A., Yavorsky, P.M., "The SYNTHOIL Process -- Material Balance and Thermal Efficiency," Paper No. 356, Bu. of Mines, Pittsburgh Energy Research Center, Dec. 1974.
7. IGT, "Preparation of a Coal Conversion Systems Technical Data Book," Final Report FE-1730-21, 1976.

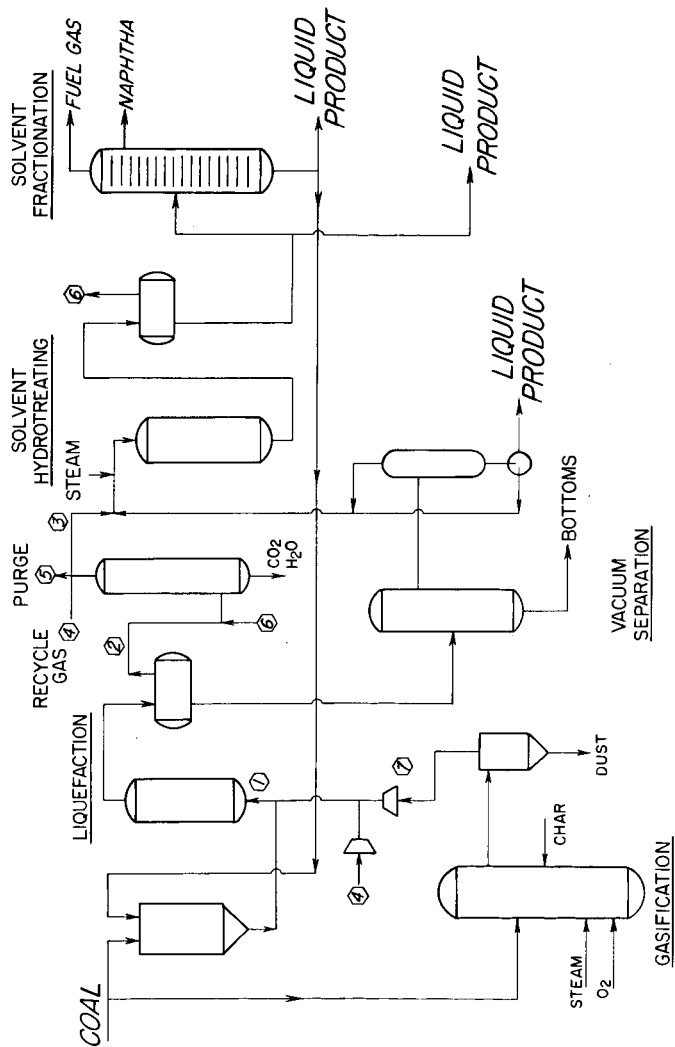


Figure 3--Solvolysis of coal using SYNGAS.

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TABLE 5. Hydrotreating of SRC Solvent
(425° C, 60 min)

	Original	Syngas (H ₂ :CO = 2:1)	H ₂
Catalyst	-	CoMo-K ₂ CO ₃	CoMo
H ₂ O added pts/100 pts		10	0
Initial Press, psi		1220	1520
Operating Press, psi		2600	2450
Product Analysis, %			
C	88.8	89.1	89.4
H	7.4	7.6	8.0
N	1.1	1.0	0.8
S	0.65	.42	.14
O	2.05	1.88	1.66
Kinematic Viscosity, CS at 60° C	12.2	7.8	5.4

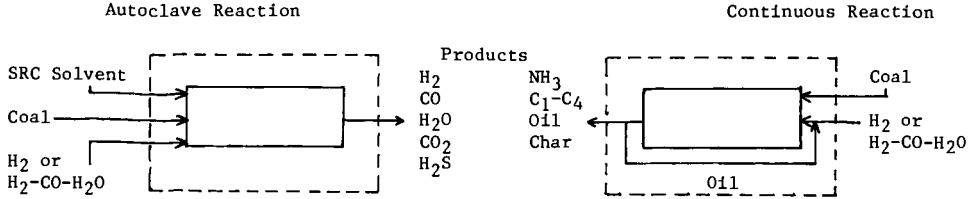
TABLE 6. Coal Liquefaction by Solvolysis

(solvent: coal = 2.3:1, 3000 psi, 450° C, 15 min)

	Syngas (H ₂ :CO = 2:1)		H ₂	
Solvent	SRC	Treated SRC	SRC	Treated SRC
Conversion, %	89	90	89	91
Asphaltene formed, %	42.7	32.6	49.3	25.6
S in oil prod., %	0.64	0.54	0.65	0.44
Kinematic viscosity, CS at 60° C	30.1	22.7	30.8	14.8

APPENDIX

Design Calculations



Elemental Balance for Continuous Reaction

Y_i = yield, (lbs of i out - lbs of i in) / lb maf coal

F_i^k = wt. fraction of element k in component i

$$C \quad F_{Coal}^C - (Y \cdot F^C)_{CO} = (Y \cdot F^C)_{C_1-C_4} + (Y \cdot F^C)_{CO_2} + (Y \cdot F^C)_{Oil} + (Y \cdot F^C)_{Char} \quad (1)$$

$$H \quad F_{Coal}^H - Y_{H_2} = (Y \cdot F^H)_{C_1-C_4} + (Y \cdot F^H)_{H_2O} + (Y \cdot F^H)_{NH_3} + (Y \cdot F^H)_{H_2S} + (Y \cdot F^H)_{Oil} + (Y \cdot F^H)_{Char} \quad (2)$$

$$O \quad F_{Coal}^O - (Y \cdot F^O)_{CO} = (Y \cdot F^O)_{H_2O} + (Y \cdot F^O)_{CO_2} + (Y \cdot F^O)_{Oil} + (Y \cdot F^O)_{Char} \quad (3)$$

$$N \quad F_{Coal}^N = (Y \cdot F^N)_{NH_3} + (Y \cdot F^N)_{Oil} + (Y \cdot F^N)_{Char} \quad (4)$$

$$S \quad F_{Coal}^S = (Y \cdot F^S)_{H_2S} + (Y \cdot F^S)_{Oil} + (Y \cdot F^S)_{Char} \quad (5)$$

Energy Balance for Continuous Reactor

H_i = net enthalpy of combustion of component i, BTU

$$\sum_i^{in} H_i T_{in} = \sum_i^{out} H_i T_{out} + \text{heat loss} \quad (6)$$

Assumptions

1. The yields of C₁-C₄ gas ($Y_{C_1-C_4}$) and char (Y_{Char}) and the elemental compositions of C₁-C₄, oil, and char observed in the autoclave experiment are used in the continuous reaction design.
2. The yield of carbon monoxide is calculated assuming the water-gas shift reaction to be at equilibrium at 477°C (28°C approach) with a H₂:CO:H₂O reactor feed of 2.05:1:0.4. It is also assumed that carbon dioxide is involved only in the water-gas shift reaction, thus $Y_{CO_2} = -Y_{CO}$.
3. The remaining unknowns are Y_{H_2} , Y_{H_2O} , Y_{H_2S} , Y_{NH_3} , and Y_{Oil} . These are determined by solving eqns. 1-5 simultaneously. The other unknown, T_{out} , is solved from eqn. 6.

Design Parameters

Oil:Coal Recycle Ratio = 2.12
 SCF/lb Slurry Reactor Feed = 15.8
 Reactor Feed Rate = 280 lb/hr-ft³ catalyst
 Reactor Inlet Temp = 425°C
 Reactor Inlet Press = 4200 psig
 Reactor Exit Temp = 449°C
 Reactor Exit Press = 4000 psig
 Process Heater Eff = 80%
 Electric Generation Eff = 40%

Economic Evaluation

Based on April 1977 CE Index
 15% Discounted Cash Flow

Hydrogen Consumption in Non-Catalyzed Coal Liquefaction

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INTRODUCTION

Liquefaction, in general, refers to the thermal reactions experienced by coals at temperature usually above 400°C in suitable solvents. These reactions produce a complex mixture of solubilized (liquefied) and gasified products in high yield over short time intervals (1). The interaction of hydrogen in these reactions is not well understood, but the presence of H₂ has been observed to increase the yields of liquefaction products (2). Hydrogen also provides a reductive pathway to allow for the removal of hetero-atoms as H₂S, H₂O and NH₃. Though the implication of these beneficial uses of hydrogen is net consumption, it has recently been shown that H₂ is also produced in these thermal reactions in non-H₂ atmospheres (3). The thermal reactions of coal in solvent, then, are best represented schematically as a set of two competing reactions (4); i.e.,

pyrolysis: coal $\xrightarrow{\text{temp}}$ H₂ + CH₄ + ... + C H_n 2n+2 + ... + aromatics + ... + coke

liquefaction: coal $\xrightarrow{\text{temp}}$ C H_n 2n+2 + ... + aromatics + ... + coke

where H₂, the light hydrocarbons and coke are maximized in pyrolysis and minimized in liquefaction. It can be seen then how hydrogen can be produced in the pyrolysis reaction, and how its presence can favor one reaction over the other without being consumed; the H₂ gas may merely inhibit the pyrolysis. Obviously, maximizing the rate of liquefaction/pyrolysis is an important consideration in the efficient use of hydrogen. We will attempt to show how each of these competing reactions respond to changing conditions and some of the effects that the various conditions produce with respect to hydrogen consumption.

EXPERIMENTAL

Data reported in this presentation have been obtained from analysis of products from 1.) a 1-liter stirred batch autoclave operating between 395°-430°C, and H₂ pressure of 1000-1750 psi measured prior to reaction at 24°C, and 2) a four-stage continuous (non-cycling) reactor operating at 425°C and 4000 psi. In the autoclave experiments, a charge of 50 g daf coal and 115 g #4 cut creosote oil was employed (5). Samples for gas analyses were obtained at ~25°C by venting through gas sampling tubes before scrubbing. The GC columns used were 6' x 1/8" O.D., 80-100 mesh poropak Q in teflon lined aluminum. The continuous reactor was packed with glass spheres; each stage was a 10 ft length, .203 inch I.D., void volume ~50%. The packing was intended to improve heat transfer and maintain mixing. The reactor was charged with a fixed slurry of #4 cut creosote oil and 30% by weight coal. The coal used in the continuous reactor was -60 mesh West Virginia, Ireland Mine coal. Block diagrams of the autoclave and reactor are shown in Figure 1a and Figure 1b. Analyses of the West Virginia, Ireland Mine coal used for both autoclave and continuous reactor experiments: ultimate (dry)

C 62.83; H 4.45; N 0.90; Cl 0.03; S 6.93; Ash 19.06; O (diff) 0.577; sulfur forms-pyrite 4.55; sulfate 0.25; organic 2.13. A description of the liquid analyses is given in block diagram form, in Figure 2. Data on other coals used in this study can be obtained from Reference 5.

RESULTS AND DISCUSSION

Comparisons of liquefaction products from different coals are not generally successful because of the variations in composition (of the coals), but can serve to illustrate the nature of the products and the role of hydrogen. Table 1 contains data from six different high volatile bituminous coals and the liquefaction products obtained in each case at 430° and .5 hour reaction times. The amount of reactive macerals varied between 89-95%, but the mineral content changed from 5 to 21%. Although the conversion varies (62-94%), the H/C ratios of the filtered (organic) products are basically the same, about 0.8. Analysis of the gas data certainly show consumption of hydrogen and production of H₂S and hydrocarbon gases. The H₂ consumption parallels conversion as does the H₂S produced. However, the production of methane, reflecting the pyrolysis reaction, does not vary in any readily apparent fashion. The H₂ consumed apparently accompanies conversion of the primary liquefaction products to benzene solubles among the several coals, as suggested by Neaval based upon the behavior of one coal in time (6).

Data obtained from the continuous reactor at 425°C shown in Table 2 clearly show two additional features of coal liquefaction 1.) the rapid initial desulfurization followed by a much slower removal of the more resistant organic sulfur; and 2.) accompanying pyrolysis reactions seen here as formation of CH₄. One conclusion based on these data is that most of the H₂S (removed sulfur) is produced in the early stages of the reactor (as is the H₂ needed for H₂S formation). Although organic sulfur is being removed, it is removed in a very specific fashion.

Reactor Stage	Asphaltene %S	Preasphaltene %S
1	1.33	1.68
2	1.24	1.59
3	1.20	1.66
4	1.22	1.68

As shown above, the percentage sulfur in the asphaltenes and the preasphaltenes is not changing significantly in time. The interconversions of the liquefaction products (as preasphaltene → asphaltene + oil) are accompanied by sulfur removal (consistent with H₂ consumption for the conversion to benzene solubles as noted earlier). Thus, sulfur removal does not occur to any significant extent without a concurrent change in solubility properties. This type of reaction is consistent with data published on hetero-atom removal from model aromatic compounds; the molecule is usually saturated with hydrogen, followed by ring opening and then removal of the hetero-atom (7). The resulting products thus, have different structures, solubility characteristics, and molecular weights and are not merely the initial molecule minus a S, N or O atom. For coal derived molecules then, this reductive cracking occurs simultaneously with defunctionalization, and both of these reactions are accompanied by hydrogen consumption.

It is necessary to examine the responses to temperature, time, and pressure to understand the process more fully. Using the same coal as in the continuous reactor, a number of autoclave experiments were performed at residence times between .25 and 1 hour, 395°-430°, and 1000-1750 psi initial pressures (pressure charges measured at 24°C before the heat cycle). Data obtained from these experiments are plotted in Figure 3, and in contrast to the data presented in Table 1, the C/H ratio of the products is changing. In Figure 3a it is seen that as time increases sulfur is removed and the amount of hydrogen in the liquefied product increases, data consistent with results drawn from the reactor runs. Likewise, sulfur decreases and hydrogen in the product increases with higher pressures, Figure 3b. However as temperature increases, the sulfur is lowered but the C/H ratio increases, Figure 3c. Figure 3d shows the amounts of H₂ gas consumed versus temperature. Though a cursory examination of Figure 3d would suggest greater hydrogenation at the higher temperature we know this is not consistent with the liquid analyses, Figure 3c. A more consistent picture is obtained by examination of the quantity of hydrogen in the gas from all sources (H₂, C₁-C₄'s, and H₂S) at two temperatures:

Gas	Moles Produced at 414°C	Moles Produced at 429°C
CH ₄	.06	.11
C ₂ H ₆	.02	.05
H ₂ S	.03	.04
H ₂ (consumed)	.30	.50

It can be seen that the total hydrogen in the gases produced is greater at higher temperature (approximately twice as large at 429° than at 414°) and indicates that temperature increases favor the pyrolysis reaction (4).

The effects observed in these experiments must not be evaluated without a description of solvent behavior under similar conditions. Table 3 shows both liquid and gas analyses of #4 creosote oil before and after reaction at 407° and 427°C. The H₂ gas consumption and CH₄ production are low compared to data obtained with coals. Also, no desulfurization is observed, though a slight increase in hydrogen content of the oil is observed. The magnitude of the differences observed in the gas data (H₂ consumption, H₂S and CH₄ formation) between the solvent and the solvents with coal would seem to indicate that the contribution of solvent to these specified (gasification and H₂ consumption) reactions was minimal (8).

SUMMARY

The discussion has considered liquefaction as two competing reactions; one which produces solubilized defunctionalized products, and a pyrolysis reaction which consumes hydrogen. Responses of the reactions to the independent variables of pressure, temperature, and time have been described and suggest that hydrogen pressure and time favor the liquefaction reactions (decreases in C/H ratio, decreases in sulfur, and increases in conversion), but that temperature seems to preferentially favor pyrolysis. These conclusions are in general agreement with

literature data. Additionally it has been shown that 1.) sulfur removal occurs concurrent with conversions among the various solvent extraction fractions, 2.) conversion varies with H_2 consumption among a number of similar but different coals and 3.) hydrogen consumption must be evaluated on the basis of a total balance, not just a change in concentration of H_2 gas.

REFERENCES

1. U.S. Bureau of Mines 646; also S. Weller, M. G. Pelipitz, E. S. Friedman, Ind. Eng. Chem. 43, 1572 (1951).
2. M. Farcasiu, T. O. Mitchell, and D. D. Whitehurst, 1st Yearly Report, RP-410-1 to EPRI (1976).
3. D. D. Whitehurst, M. Farcasiu, T. O. Mitchell, and J. J. Dickert, Jr., 2nd Yearly Report, RP-410-1 to EPRI (1977).
4. W. H. Wiser, L. L. Anderson, S. A. Quaged, G. R. Hill, J. Appl. Chem. Biotechnol. 21, 82 (1971).
5. Barry Granoff and Michael G. Thomas, Preprints, Div. of Fuel Chemistry, Amer. Chem. Soc., 22 (6), 183 (1977).
6. R. C. Neavel, Fuel, 55, 237 (1976).
7. M. Houalla, D. Brodirich, V. H. J. De Deer, B. C. Gates, H. Kwart, "Structure and Reactivity," Preprints, Petroleum Chemistry Symposia, Amer. Chem. Soc., March 1977.
8. Arthur R. Tarrer, James A. Guin, Wallace S. Pitts, John P. Henley, John W. Prather and Gary A. Styles, Preprints, Div. of Fuel Chem., 21 (5) 59 (1976).

FIGURE 1. BLOCK DIAGRAMS OF a. AUTOCLAVE, AND b. 4-STAGE REACTOR.

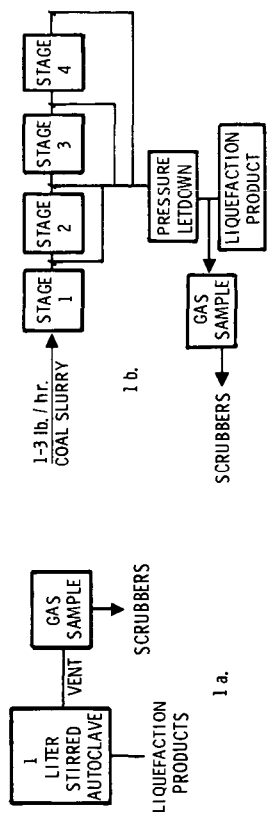


FIGURE 2. BLOCK DIAGRAM OF LIQUID ANALYSIS.

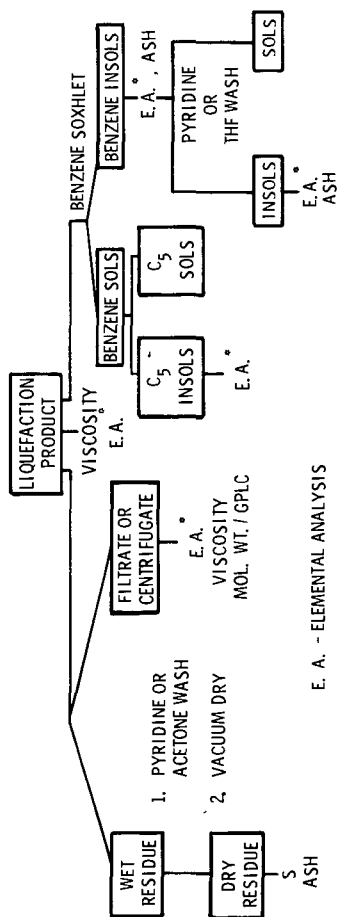


Table 1. Selected data of several coals and respective liquefaction products.

	Coal %S	Reactive Macerals	Mineral Matter	Conv.	OBI	Filtered Product H/C	Mole % H ₂ S	Mole % CH ₄	Moles H ₂ Consumed
Kent. 11, Fies	6	93	20.9	93	7.8	.82	6.6	2.87	.57
Kent. 11, Homestead	4.76	92	15.7	94	10.3	.83	3.2	2.71	.53
West Va.	4.03	91	13.8	88	10.6	.80	2.44	3.70	.41
Ill. 6	2.91	95	13.0	87	14.8	.80	1.62	2.16	.40
Pennsylvania	1.03	90	5.2	84	16.5	.81	0.38	1.82	.33
Kent. Elkhorn 3	.78	89	5.6	62	22.9	.81	0.36	1.85	.31

Table 2. Reactor products from a run at 425°C, 4000 psi H₂, 1 lb/hr coal.

	Product %S	Benzene Insols	Asphaltene	THF Preasphaltene	% of Total S in THF Insols	Moles CH ₄ / lbs. Coal
Reed	1.40	30.0	-	-	92.0	-
Stage 1	1.07	18.9	11.8	9.9	39.0	.68
Stage 2	.83	15.4	13.1	8.5	40.5	1.47
Stage 3	.86	10.9	15.5	5.3	-	2.18
Stage 4	.81	9.8	13.4	4.8	40.8	3.10

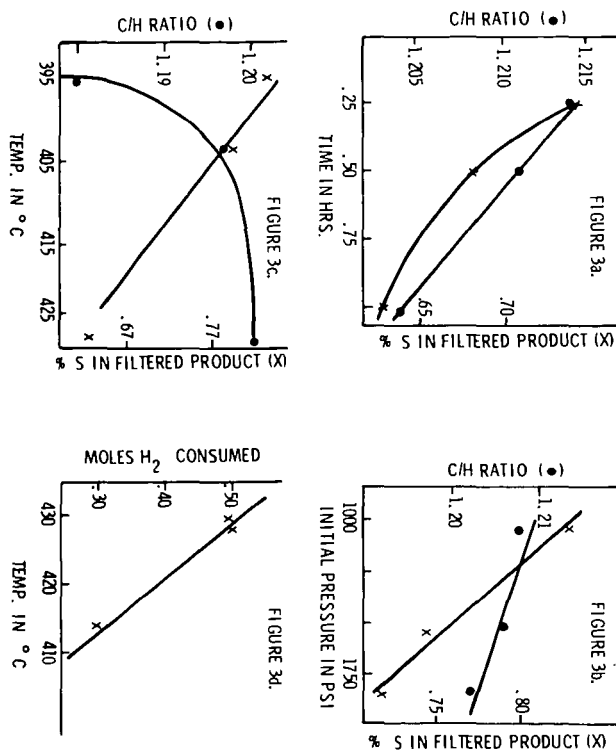


FIGURE 3. a. C/H RATIO AND S vs. TIME (430°C, Initial H₂ Pressure 1500 psi)
 b. C/H RATIO AND S vs. PRESSURE (405°, time 1 hour)
 c. C/H RATIO AND S vs. TEMPERATURE (time 1 hour, Initial H₂ Pressure 1500 psi)
 d. MOLES H₂ CONSUMED vs. TEMPERATURE (time and Pressure as in 3c)

Table 3. Analyses of #4 Cut Creosote Oil

	Initial	1800 psi, .5 hr 407°	1800 psi, .5 hr 427°
Pyridine Insols	0.0	0.0	0.0
Benzene Insols	0.3	1.0	1.6
Asphaltene	7.3	3.9	3.2
Oil	92.7	95.1	95.2
C	90.77	91.03	-
H	5.8	5.93	-
S	.4	.4	.4
Moles CH ₄	-	.0029	.0097
Moles H ₂ Consumed	-	.004	.015

CONCEPT AND USE OF HYDROGEN PERMEABLE CATALYSTS

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INTRODUCTION

The concept of a hydrogen-permeable catalyst has not previously been reduced to practice for any gaseous or liquid mixture of coal-derived compounds, including sulfur compounds. The only known instance of the use of this concept is that described in a U.S. Patent by Rudd (1). In his work hydrogen was diffused under pressure through a palladium coil into a vessel containing ethylene. The ethylene was readily reduced to ethane, presumably by reaction with the hydrogen at the palladium surface, the palladium acting as a catalyst. The hydrogen for this reaction was apparently limited to that which had diffused just to the surface of the palladium, and was present as atomic hydrogen. In another experiment, Rudd demonstrated that an oxide coating produced on one side of a Hastelloy B disc could be completely removed by diffusing hydrogen through the disc from the non-oxidized side. The self-cleaning effects of a hydrogen permeable catalyst are implied in this demonstration, although Rudd did not try to use Hastelloy B as a catalyst.

The successful implementation of the concept of hydrogen permeable catalysts to coal-derived gases or liquids, and even coal or coal/recycle oil slurries, may offer several technical and economic advantages. These could include the virtual absence of unused hydrogen that has to be purified, recompressed and recycled at considerable expense, because essentially all the hydrogen could be consumed at the catalyst surface, without forming hydrogen bubbles. Another advantage, as suggested by Rudd's work, is that the catalyst surface could be kept free of carbon deposits because, just as oxides were removed by reaction with hydrogen diffusing up through the metal, so coking precursors would be converted by hydrogenation, preventing the formation of carbonaceous deposits. Finally, it may be possible to prevent the buildup of mineral deposits when coal or coal slurries are used, because the presence of a mono-molecular or monoatomic layer of hydrogen at the surface would prevent the adhesive forces between the mineral particles and the catalyst surface from being effective.

EXPERIMENTAL PROCEDURE

Reactor Design and Function

The general reactor design is briefly as follows. The shell of the hydrogen permeable catalyst reactor consisted of 3-inch O.D. schedule 80 stainless steel pipe, 4-feet and 7-inches in length. One end of the pipe was adapted to accept tubing from one inch to 3/8 inches in diameter. The other end was modified to accept tubing from 1/2 to 3/8 inches in diameter. One quarter inch openings were made in the reactor walls to permit inlet and venting of gases. Catalyst tubes were connected at each end to short lengths of stainless steel tubing. The stainless steel tubing, holding the catalyst tube, was inserted into the reactor at the end containing the larger opening, and allowed to protrude from the lower end of the reactor for a length of about 8 inches. The reactor, containing the catalyst tube, was suspended vertically in a high temperature furnace. Connections were made to the walls of the shell to permit inlet and venting of gases. Connections were made to the stainless steel tubing at the bottom of the reactor to permit hydrogen sulfide and hydrogen

for presulfiding, and liquid feed to enter the tube, with appropriate valving. The upper end of the tube went directly into a product receiver (gas liquid separator). Lines from the gas-liquid separator were connected to a cold trap, and then into a wet test meter for measuring any gas flow.

Hydrogen Permeable Catalyst Tubes

The thin-wall nickel-200 tubing was composed of 99.5 wt. % Ni, with small amounts of iron and manganese. Dimensions of the tubes were 17-7/8 inch length by 3/8-inch O.D., with wall thickness reduced from 0.035-inch to 0.017-inch to a point approximately one inch from each end. Samples of finely porous nickel-molybdenum and cobalt-molybdenum tubing were fabricated at Oak Ridge National Laboratory from micron-range powders by flame spraying on a mandrel, followed by high-temperature sintering to densities in excess of 95% of the natural density. The dimensions after sintering were 16.5-inches length, 0.181-inches I.D., and 0.396-inches O.D. The total length was 21-inches after brazing on nickel tips for ease of mounting in the reactor.

Catalyst tube permeability measurements were made by determining the hydrogen flow from the shell side through the permeable tubing by the wet test meter connected to the tube side of the reactor.

The internal surfaces of all catalyst tubes were coated with a metal sulfide layer by passage of a 50% hydrogen sulfide and 50% hydrogen mixture through the tube for four hours at a catalyst tube temperature of 400°C. After sulfiding, the entire reactor system was cooled to 100°C, purged with nitrogen to remove all traces of hydrogen sulfide.

Hydrogenation of liquid feed was accomplished by pumping the feed at a predetermined rate up through the catalyst tube to react with hydrogen diffusing from the shell through the catalyst tube wall. Experimental runs were made at catalyst tube temperatures from 250°C to 450°C and shell side pressures of 655 psig hydrogen to 1510 psig hydrogen. Hydrogen pressures inside the tube varied from 650 psig to 1,495 psig. Temperatures inside the tube were determined with a thermocouple in an axially positioned well.

Analyses

The identities of the metal sulfides were determined by x-ray diffraction analysis, while the compositions of the liquid feeds and liquid products, and the composition of the gaseous products, were determined by gas chromatography/mass spectrometry, and gas chromatography. Other analyses were employed, as required. The hydrogen permeability values for nickel metal are known (2).

DISCUSSION OF RESULTS

Thin Wall Nickel Tubing Reactors

1. Runs with Tar Oil in Ni Tubes. X-ray diffraction analyses of the various samples of sulfided nickel tubing showed that in each instance the coating on the inner wall consisted of a mixture of Ni_3S_4 and Ni_3S_2 . The latter compound, nickel subsulfide, was very likely the only form present soon after the start of each hydrogenation run. According to Weisser and Landa (3) all nickel sulfides are rapidly converted to the subsulfide by hydrogen in any use of the sulfides for hydrogenation reactions. In any event, a large amount of Ni_3S_2 was observed for both the fresh and used tubing. Weisser and Landa also describe the use of nickel subsulfide as a catalyst for hydrogenation, including the hydrogenolysis of thiophene-type compounds. That the Ni_3S_2

present was actually functioning as a catalyst was demonstrated by the decreases in the amounts of six major components of the feed, and the increases in the amounts of eleven probable product compounds, as shown in Table 2 for runs 1 through 5, according to the conditions shown in Table 1. The reactants, R, and probable products, P, are arranged into four groups, following the possible reaction mechanisms shown in Figure 1. The reaction intermediates, indicated in Figure 1 by brackets, were not detected. All other compounds shown were identified, and their amounts determined, by combined gas chromatography and mass spectrometry. The observed m/e values are given in Table 2, along with the number of millimoles of each compound per 100 g sample, and the change in millimoles per 100 g sample in going from the feed to the product. No benzothiophene was added to the feed in run 4.

Most of the possible reaction mechanisms shown in Figure 1 for the thin-wall nickel tubing reactors have been studied in depth by other researchers under various conditions other than with nickel subsulfide catalyst. Qader and Hill (4) have shown the sequence naphthalene \rightarrow tetralin \rightarrow methylindan \rightarrow indan \rightarrow alkylbenzene. Penninger and Slotboom (5) have further detailed the steps leading from tetralin to alkylbenzenes. Rollman (6) has defined the steps in the conversion of benzothiophene to alkylbenzene, as have Furinsky and Amberg (7). Oltay *et al.* (8) have shown the steps in the conversion of 2-methylnaphthalene to tetralin and alkylbenzene as have Qader *et al.* (9). The two conversion sequences: 1) phenanthrene \rightarrow dihydrophenanthrene \rightarrow ethylbiphenyl \rightarrow biphenyl; 2) phenanthrene \rightarrow tetrahydrophenanthrene \rightarrow alkylnaphthalene \rightarrow tetralin have been detailed by Wu and Haynes (10). The sequence fluorene \rightarrow methylbiphenyl \rightarrow biphenyl has been shown by Oltay *et al.* in a second paper (11), as well as Penninger and Slotboom (5).

The hydrogen permeable catalyst tube in run 2, which was regenerated with air oxidation after being used in run 1, and then resulfided, showed the greatest activity of the five tubes used. The lowest activity was shown for the tube in run 1, lower than the tubes used in runs 4 and 5, which were not presulfided with the $H_2 + H_2S$ mixture. In these latter two runs a more effective nickel subsulfide coating was obtained by the reaction of the organic sulfur compounds present in the tar oil (0.64 weight percent sulfur), and the reaction of the benzothiophene added to the tar oil feed. The small amount of sulfur in the tar oil was as effective in run 4 as was the much larger amount of benzothiophene added to the tar oil in run 5. The used tubes from all runs did not have any noticeable carbon deposits, even after 13 hours operation. The relatively low operating temperature of 400°C was probably helpful in this regard, and it seems reasonable to assume that the cleansing action of the diffusing hydrogen, as described by Rudd (1), was operative. Only small amounts of hydrocarbon gases were detected in the gas in the tubing, indicating that limited cracking has occurred, whether hydrocracking or thermal cracking. Typical concentrations observed were 0.14 volume percent methane and 0.03 volume percent ethane, the remainder being the hydrogen required to maintain the 1,000 psig tube-side pressure.

2. Runs with Pure Compounds in Ni Tubes. A series of six test runs (runs 6 through 11) on the hydrogen permeability of thin wall nickel-200 tubing at various temperatures and differential pressures, and on the degree of hydrogenation of four different pure polycyclic aromatic compounds used as model compounds was likewise conducted. The hydrogen diffusivities were measured from the shell side to the inner tubing side over the shell to tubing pressure differential range of 300 to 1,700 psig, and temperatures of 400° and 450°. At both temperatures the amount of hydrogen diffusing through the wall at a Δp of 300 psig was essentially zero. The H_2 flow through the wall increased rapidly with increasing Δp , leveling off at about 0.45 liters/hr at 400°C and 1,500 psig Δp , and about 0.65 liters/hr at 450°C and 1,700 psig Δp .

The inside of the nickel tubing was sulfided by reacting at 400°C with about 8 cu. ft. of a 50-50 mixture of hydrogen sulfide and hydrogen. X-ray diffraction analysis showed the principal component to be nickel subsulfide. The inner surface was covered with a very rough texture of tiny, dark grey crystallites of this

material. There was no significant decrease in hydrogen permeability after sulfiding. Benzothiophene was added to all liquid feeds in order to ensure maintenance of this sulfided surface. SEM analysis gave 0.2 μm as a typical crystallite size.

Phenylcyclohexane was chosen as the solvent for the model compounds because of its presumed relative inertness and because it is a liquid at room temperature. Runs were made with about 5 to about 13 weight percent of each of the four model compounds dissolved in this solvent. The Δp was 700 or 750 psig, with the inner tube pressure about 1,000 psig. Temperatures of 290, 340, 400 and 450°C were used, generally with a feed residence time of about 1 hour, and usually somewhat less than the stoichiometric hydrogen required for complete hydrogenation of the components present. Table 3 shows the results for gas chromatographic analyses of the products. There was a general trend to greater hydrogenation with higher temperature and longer residence time, as would be expected.

Porous Nickel-Molybdenum Reactors

1. Runs with Pure Compounds in Ni-Mo Tubes. The run conditions are summarized in Table 4 for the Ni-Mo tubing reactors. The results for the gas chromatographic analysis of the receiver product for runs 12 and 13 with pure compounds are shown in Table 5. At low hydrogen pressure (650 psig) inside the tubing, with about 4.5 psig differential pressure for diffusing the hydrogen through the pores of the tubing from the shell side, there was substantial reaction of the phenanthrene (45% conversion) and the benzothiophene (27% conversion). Biphenyl in the product probably came from hydrogenolysis of dihydrophenanthrene. The alkylbenzenes came in part from the phenanthrene and benzothiophene but probably also from hydrogenolysis of the solvent, phenylcyclohexane. High yields of alkylbenzenes were obtained in the thin-wall nickel tube runs in the absence of phenylcyclohexane (Table 2). At the higher hydrogen pressure (1,350 psig) enough of the intermediate di- and tetrahydrophenanthrenes were produced to be detected, and the amount of biphenyl increased. The apparent increase in the amounts of phenanthrene and benzothiophene was due to loss of volatiles, probably mostly benzene, as shown by the unexpectedly low yield of this product. As will be seen for the results from the comparable runs at these pressures with tar oil as feed, the most reasonable estimate is that the amount of conversion was doubled upon doubling the pressure, as indicated by the yields of toluene, xylenes, and biphenyl.

In two runs with pure compounds, designated 13-S and 14-S, at the run conditions shown for runs 13 and 14 in Table 4, product from the top (exit) end of the catalyst tube drained down the outside of the tube into the cold lower portion of the pressurized shell, from which it was drained at the conclusion of the run, rather than from the product receiver. It was observed in these runs under these particular operating conditions there was even greater conversion to benzene, alkylbenzenes, and biphenyl. The dihydrophenanthrene was largely converted to biphenyl under these conditions, but in so doing the intermediate methylbiphenyl was produced in large enough amount for detection. The amount of conversion was increased upon decreasing the LHSV from 20.0 to 13.3, i.e., upon increasing the residence time from 3.0 to 4.5 minutes, as indicated by the yields of toluene, xylenes, and biphenyl. The production of naphthalene in this run would indicate the formation of the intermediate tetrahydrophenanthrene, but none could be detected.

2. Runs with Tar Oil Feed in Ni-Mo Tubes. The results for the gas chromatographic analysis of the receiver product for runs 15 and 16 with coal tar creosote oil feeds are shown in Table 6. In run 15 considerable total hydrogen sulfide was evolved, showing that the 0.6 wt. % sulfur in the feed was insufficient to maintain a heavy sulfide coating inside the nickel-molybdenum tubing. This was probably because the hydrogen permeability of the Ni-Mo tubing was so high as indicated by the pressure differentials of only 5 to 10 psig (Table 4), compared to 700 psig for the thin-wall nickel tubing (Table 1). Nevertheless, a significant conversion of various feed components was observed. MoS_2 , molybdenum disulfide, a known hydrogenation catalyst,

was present in the Ni-Mo tube, as well as Ni_3S_2 . The presence of MoNi_4 alloy was also shown.

Analysis of the product gas from run 15 showed 0.29 vol. % hydrogen sulfide, whereas the gas from run 16 had no detectable H_2S , showing that the metal sulfide layer had stabilized with the small sulfur content of the feed. The hydrocarbon in largest quantity in the gas from run 15 was propane at 0.14 vol. %. This would seem to indicate hydrocracking of the saturated rings of hexahydropyrene to yield propane and naphthalene, or propane, ethane, and methyl-naphthalene. Table 6 shows that the primary product was methyl-naphthalene in run 15. The product gas from run 16 showed methane at 2.67 vol. %, and ethane at 0.26 vol. % to be the hydrocarbon gases in the largest quantities. This would seem to indicate hydrocracking of the saturated rings of tetrahydroacenaphthene to produce these gases and alkylbenzenes. Table 6 shows that the primary reactant was acenaphthene, with tetrahydroacenaphthene and alkylbenzene the major products.

These possible reaction mechanisms, and others, are shown in Figure 2. The hydrogenated derivatives of pyrene and fluoranthene could not be detected, and so are shown in brackets. However, tetrahydroacenaphthene (Table 6), dihydrophenanthrene (Table 5), and tetrahydrophenanthrene (Table 5) were all found in significant quantities when using the porous nickel-molybdenum tubing reactors. The only reasonable source for the pentane found by GC would be the hydrocracking of phenylcyclohexane. Qader and Hill (4) have shown the sequence pyrene \rightarrow hydroxyrenes \rightarrow naphthalenes \rightarrow tetralin \rightarrow benzenes. As mentioned previously, Wu and Haynes (10) have outlined the two conversion sequences for phenanthrene. Fluoranthene also has the sequence leading to tetrahydrofluoranthene and then, by hydrocracking, to methylbiphenyl.

Porous Cobalt-Molybdenum Reactors

Runs were made using the porous cobalt-molybdenum tubing fabricated at ORNL and pure compounds (phenanthrene and benzothiophene) dissolved in phenylcyclohexane. The inner surface of the tubing was sulfided before use in the same manner as for the nickel-molybdenum tubing. The operating conditions and the results for gas chromatographic analysis of the products, are summarized in Table 7.

The respective run numbers, weight of feed material (g), pump rate (g/hr), and total run time (hr) were: 17, 32.82, 45, 2.00; 18, 189.4, 50.49, 2.25; 19, 239.2, 26.3, 2.50. The hydrogen flows for the Co-Mo reactors were very similar to those for the Ni-Mo reactors, the respective run numbers, average hydrogen flow (l/hr), and total hydrogen flow (l) being: 17, 4.7, 9.4; 18, 7.2, 16.3; 19, 5.64, 14.1.

A comparison of the results for the porous Ni-Mo reactors in Table 5 with those for the porous Co-Mo reactors in Table 7 shows that the reactions of the pure compounds were similar, but the sulfided Co-Mo appeared to have a little greater activity than the sulfided Ni-Mo, at the same approximate temperature and pressure, for the production of dihydrophenanthrene and its hydrocracking products, dimethylbiphenyl, methylbiphenyl, and biphenyl, and the production of tetrahydrophenanthrene, and its cracking product, naphthalene.

Hydrogen Permeability

It was not possible to measure hydrogen permeability of thin-wall nickel tubing during a run, because of the relatively low rate of hydrogen flow, and permeabilities had to be measured beforehand with the empty tubing, making hydrogen stoichiometry calculations difficult. However, direct hydrogen flow measurements could be made during the runs with the porous nickel-molybdenum tubing (Table 4) for comparison with the amounts required for any presumed set of hydrogenation reactions. Neglecting certain reactions, such as the hydrocracking of the phenylcyclohexane solvent, from 54 to 89% of the available hydrogen was consumed in the pure compound runs, and 85

to 90% in the tar oil runs. When estimations are allowed for these neglected reactions, it appears that essentially all hydrogen was consumed except that required to maintain pressure on the inside of the tubing. The high hydrogen flow rates with the porous Ni-Mo tubing allowed economically low feed residence times of only 3.0 to 12.6 minutes. A similar situation existed for the Co-Mo tubing.

As long as hydrogen flow was maintained through the tubing wall, there was never any indication of carbon deposits, even after many hours use on successive runs. However, in one instance, at the termination of run 16 at 400°C, the pressure differential of 10 psig H₂ from the shell-side to the tubing-side was lost, allowing the tar oil feed to penetrate the pores under conditions of poor contact with hydrogen. A heavy carbonaceous deposit was produced, typical of extensive cracking.

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REFERENCES

1. Rudd, David W., "Apparatus for Use in Effecting Chemical Reactions," U.S. Patent 3,210, 162, Oct. 2, 1965.
2. International Critical Tables, Vol. 5, p. 76, McGraw-Hill Book Co., Inc., NY, 1933.
3. Weisser, Otto, and Stanislav Landa, "Sulfide Catalysts, Their Properties and Applications," Pergamon Press, NY, 1973.
4. Qader, S.A., and G.R. Hill, "Development of Catalysts for the Hydrocracking of Polynuclear Aromatic Hydrocarbons," Amer. Chem. Soc., Div. Fuel Chem. Prepr. 1972, vol. 16, no. 2, pp. 93-106.
5. Penninger, Johannes M.L., and Hendrik W. Slotboom, "Mechanism and Kinetics of the Thermal Hydrocracking of Single Polyaromatic Compounds," Chap. 25 in "Industrial and Laboratory Pyrolysis," L.F. Albright and B.L. Crynes, eds., ACS Symposium Series 32, Amer. Chem. Soc., Washington, DC, 1976, pp. 444-456.
6. Rollman, Louis D., "Competitive Hydrogenation of Model Heterocycles and Polynuclear Aromatics," Amer. Chem. Soc., Div. Fuel Chem. Prepr. 1976, vol. 21, no. 7, pp. 59-66.
7. Furimsky, E. and C.H. Amberg, "The Catalytic Hydrodesulfurization of Thiophenes. VIII. Benzo thiophene and 2,3-Dihydrobenzothiophene," Can. J. Chem., vol. 54, no. 10, 1507-1511 (1976).
8. Oltay, Ernst, Johannes M.L. Penninger, and Peter G.J. Koopman, "Thermal High-Pressure Hydrogenolysis of 2-Methylnaphthalene," Chimia, vol. 27, no. 6, 318-19 (1973).
9. Qader, S.A., L. Chun Chen, and D.B. McOmber, "Hydrocracking of Polynuclear Aromatic Hydrocarbons over Mordenite Catalysts," Amer. Chem. Soc., Div. Petrol. Chem. Prepr. 1973, vol. 18, no. 1, pp. 60-71.
10. Wu, Wen-Lung and H.W. Haynes, Jr., "Hydrocracking Condensed-Ring Aromatics Over Nonacidic Catalysts," Chap. 4 in "Hydrocracking and Hydrotreating," J.W. Ward and S.A. Qader, eds., ACS Symposium Series 20, Amer. Chem. Soc., Washington, DC, 1975, pp. 65-81.
11. Oltay, Ernst, Johannes M.L. Penninger, and Willem A.N. Konter, "Thermal High Pressure Hydrogenolysis. II. The Thermal High Pressure Hydrocracking of Fluorene," J. Appl. Chem. Biotechnol., vol. 23, 573-579, 1973.

TABLE 1. Operating Conditions for Thin-Wall Nickel Tubing
Hydrogen Permeable Catalyst Reactors

Hydrogenation Run No.	1	2	3	4	5
H ₂ Permeability of Cat. Tube - 700 psig Diff. & 400°C, cc/min	0.77	0.72	0.68	1.83	1.83
Dry Air Oxidation of Catalyst Surface	Non Oxidized	Oxidized 4 Hrs. @ 400°C	Non Oxidized	Non Oxidized	Non Oxidized
Sulfiding Conditions - Internal Surface of Tube	50% H ₂ + 50% H ₂ S 4 Hrs. @ 400°C	50% H ₂ + 50% H ₂ S 4 Hrs. @ 400°C	50% H ₂ + 50% H ₂ S 4 Hrs. @ 400°C	Non Sulfided Sulfided by Feed Oil	Non Sulfided at Start of Run
H ₂ Permeability of Cat. Tube - 700 psig, 400°C after sulfiding, cc/min	0.79	0.93	0.57	1.83	1.83
Feed Raw Material	Clean Reilly Tar Oil + Ben- zothiophene	Clean Reilly Tar Oil + Ben- zothiophene	Clean Reilly Tar Oil + Ben- zothiophene	Clean Reilly Tar Oil	Benzothio- phene Mod- ified Reilly Tar Oil
Wt. of Feed Material, g	151.80	131.89	146.76	142.00	187
Pump Rate, cc/hr	7.04	10.65	8.90	15.33	11.49
Catalyst Tube Temperature °C	400	400	400	400	400
Pressure Differential (shell to tube) psig - H ₂	700	700	700	700	700
Tube Side Pressure, psig	1,000	1,000	1,000	1,000	1,000
Residence Time in Catalyst Tube, Hrs.	2.87	1.90	2.27	1.32	1.62
LHSV	0.35	0.53	0.44	0.76	0.62
Total Run Time, Hrs.	12.27	9.0	12.0	9.33	13.08

TABLE 2. Amounts of Reactant and Product Compounds in Feed Oil and Product from Ni Hydrogen Permeable Catalyst Tube; 400°C; 1,000 psig Tube Side

Millimoles/100 GRAMS

COMPOUND	m/e	Feed Oil + Benzothiophene	Run 1 Product 0.35%	Change ²	Run 2 Product 0.53%	Change	Run 3 Product 0.44%	Change	Run 4 Product 0.76%	Change	Run 5 Product 0.62%	Change
Naphthalene (R) ¹	128	46.8	37.5	- 9.1	34.06	-12.74	35.00	-11.8	34.37	-18.47	32.19	-14.61
1-Benzothiophene (R)	134	90.3	8.95	-81.3	8.13	-82.17	8.20	-82.10	0.0	0.0	7.68	-82.62
Benzene (P)	78	0.0	0.26	+ 0.26	3.46	+ 3.46	0.89	+ 0.89	1.41	+ 1.41	1.79	+ 1.79
Toluene (P)	92	0.54	2.06	+ 1.52	13.47	+12.93	3.04	+ 2.50	5.65	+ 5.11	7.17	+ 6.63
Xylenes & Ethylbenzene (P)	106	0.0	2.17	+ 2.17	2.73	+ 2.73	3.11	+ 3.11	2.83	+ 2.83	2.45	+ 2.45
Trimethylbenzenes (P)	120	0.08	2.75	+ 2.67	1.83	+ 1.75	1.91	+ 1.83	1.83	+ 1.74	1.58	+ 1.50
2-Methylnaphthalene (R)	142	37.6	25.5	-12.1	24.64	-12.96	22.11	-15.49	21.05	-21.34	22.60	-15.00
Ethylindan (P)	146	0.0	2.39	+ 2.39	2.19	+ 2.19	2.53	+ 2.53	2.67	+ 2.67	2.26	+ 2.26
Indan (P)	118	2.54	3.60	+ 1.06	4.41	+ 1.87	3.05	+ 0.51	3.64	+ 0.77	3.64	+ 1.10
Acenaphthene (R)	154	49.0	33.11	-15.9	30.84	-18.16	27.53	-21.47	29.09	-26.28	29.67	-19.33
Ethyl-naphthalenes (P)	156	4.67	9.20	+ 4.53	10.77	+ 6.1	10.12	+ 5.45	9.23	+ 3.96	10.00	+ 5.33
Dimethylnaphthalenes (P)	156	17.1	22.8	+ 5.70	25.32	+ 8.22	26.79	+ 9.69	25.00	+ 5.68	23.78	+ 6.68
Fluorene (R)	166	36.9	28.2	- 8.70	26.44	-10.46	24.39	-12.51	24.75	-16.94	25.96	-10.94
Phenanthrene (R)	178	90.7	47.8	-42.9	41.23	-49.47	35.88	-54.82	37.75	-64.74	40.56	+50.14
Methylbiphenyls (P)	168	3.33	13.1	+ 9.77	17.79	+14.46	17.62	+14.29	14.46	+10.7	16.72	+13.39
Biphenyl (P)	154	8.31	12.3	+ 3.99	13.31	+ 5.0	13.11	+ 4.8	12.46	+ 3.07	12.59	+ 4.28

¹R = Reactant, P = Product

²+ = Increase, Feed to Product; - = Decrease, Feed to Product

³1-Benzothiophene Free Reilly Tar Oil Feed Used In Run 4

⁴LHSV (Liquid Hourly Space Velocity)

TABLE 3. Reaction of Diffused Hydrogen with
Pure Compounds in Thin Wall Ni Tubing
with Ni₃S₂ Coating, about 1,000 PSIG

Solvent = Phenylcyclohexane

Run No.	Temp., °C	LHSV	Compound	Weight %		
				Feed	Product	Hydrogenated
6	290	1.0	Benzothiophene	5.74	4.68	19
7	290	1.0	Phenanthrene	7.58	6.36	16
			Benzothiophene	6.22	5.11	18
8	290	1.0	Acenaphthene	7.67	4.98	35
			Benzothiophene	6.25	5.63	10
9	340	1.0	Fluorene	7.79	5.13	21
			Benzothiophene	6.09	5.30	13
10	400	1.2	Phenanthrene	12.97	7.70	41
			Benzothiophene	7.06	4.79	32
11	450	0.51	Phenanthrene	5.21	2.62	50
			Benzothiophene	5.10	2.23	56

TABLE 4. Operating Conditions for Porous Nickel-Molybdenum Tubing Hydrogen Permeable Catalyst Reactors at 400°C

Run No.	12	13	14	15	16
Sulfiding Conditions, Internal Surface	50% H ₂ + 50% H ₂ S, 4 hours at 400°C, total gas flow = 8 feet ³				
Feed Material	Phenylcyclohexane, Phenanthrene Benzothiophene (various proportions)				Filtered Reilly Tar Oil
Wt. of Feed Material, g	150.0	160.1	205.2	267.7	114.4
Pump Rate, g/hr	56.2	64.0	41.0	48.6	57.2
Total Run Time, hrs	1.63	1.25	1.5	1.9	2.0
Residence Time in Catalyst Tubing, min	3.0	3.0	4.5	12.6	10.2
Pressure Inside Tubing, psig	650	1,350	1,350	767	1,380
Pressure Differential (shell to tubing), psig	4.5	10.0	10.0	8.5	10.0
Hydrogen Flow, liters/hr	6.26	5.56	4.50	5.40	5.10

TABLE 5. Reaction of Pure Compounds at 400°C with Hydrogen Diffusing Through Porous Nickel-Molybdenum Tubing with a Sulfided Inner Wall

Feed: 4.52 wt. % benzothiophene
10.17 wt. % phenanthrene
(solvent: phenylcyclohexane)

Run No.	Receiver Product, Wt. %	
	12	13
Pressure, psig	650	1350
LHSV	20.0	20.0
Benzene	16.56	0.69
Toluene	0.63	1.49
Xylenes	1.77	3.33
Trimethylbenzenes	0.06	0.97
Biphenyl	0.58	1.28
Dihydrophenanthrene	0.00	2.26
Tetrahydrophenanthrene	0.00	1.09
Phenanthrene	5.60	12.03 ¹
Benzothiophene	3.29	7.97 ¹

¹High, due to loss of volatiles, mostly benzene.

TABLE 6. Reaction of Coal Tar Creosote Oil at 400°C with Hydrogen Diffusing Through Porous Nickel-Molybdenum Tubing with Sulfided Inner Wall

Composition, Weight %						
Run No.	15			16		
LHSV	4.8			5.9		
Pressure, psig	767			1,380		
Reactants	Feed	Receiver Product	Decrease	Feed	Receiver Product	Decrease
Acenaphthene	8.61	8.45	0.16	8.23	4.03	4.20
Phenanthrenes ¹	20.01	19.06	0.95	20.77	18.44	2.33
Pyrene	6.68	4.30	2.38	5.59	3.52	2.07
Fluoranthene	5.83	4.81	1.02	5.99	4.09	1.90
Total			4.51			10.50
Products	Increase			Increase		
Benzene	0.00	0.21	0.21	0.00	1.52	1.52
Toluene	0.10	0.10	0.00	0.33	2.22	1.89
Xylenes	0.16	0.20	0.04	0.21	2.03	1.82
Indan	1.23	1.57	0.34	1.99	3.06	1.07
Tetralin	1.15	1.60	0.45	1.45	2.15	0.70
Methylnaphthalenes	11.70	14.56	2.86	9.29	10.91	1.62
Tetrahydroacenaphthene	0.00	0.34	0.34	0.00	1.85	1.85
Total			4.24			10.47

¹Phenanthrene plus methylphenanthrenes.

TABLE 7. Reaction of Pure Compounds with Hydrogen
Diffusing Through Porous Cobalt-Molybdenum
Tubing with Sulfided Inner Wall

Solvent = Phenylcyclohexane

Run No.	17	18	19
Temp., °C	350	400	400
Pressure inside tube, psig	750	728	1,495
Pressure, diff- erential, psig	20	9.0	7.0
Residence time, min.	11.4	10.2	19.2
LHSV	5.3	5.9	3.1

Composition, Weight %

	Feed	Product	Feed	Product	Feed	Product
Pentane	0.00	0.00	0.00	2.73	0.00	0.00
Benzene	0.64	6.91	0.60	7.54	1.75	0.03
Toluene	0.00	0.02	0.00	4.73	0.00	0.08
Xylenes	0.00	1.93	0.00	6.36	0.00	1.74
Trimethylbenzenes	0.00	0.00	0.00	1.13	0.00	0.59
Naphthalene	0.00	0.62	0.00	4.68	0.00	2.20
Biphenyl	0.00	0.00	0.00	3.46	0.00	4.49
Methylbiphenyl	0.00	0.00	0.00	0.00	0.00	0.99
Dimethylbiphenyl	0.00	0.00	0.00	0.00	0.00	1.12
Dihydrophenanthrene	0.00	0.00	0.00	0.05	0.00	5.97
Tetrahydrophenanthrene	0.00	0.00	0.00	0.00	0.00	2.08
Phenanthrene	11.82	5.05 ¹	12.12	5.70 ¹	13.28	23.74 ¹
Benzothiophene	4.42	4.42 ¹	4.51	5.40 ¹	5.27	5.28 ¹

¹High, due to loss of volatiles, primarily pentane and benzene.

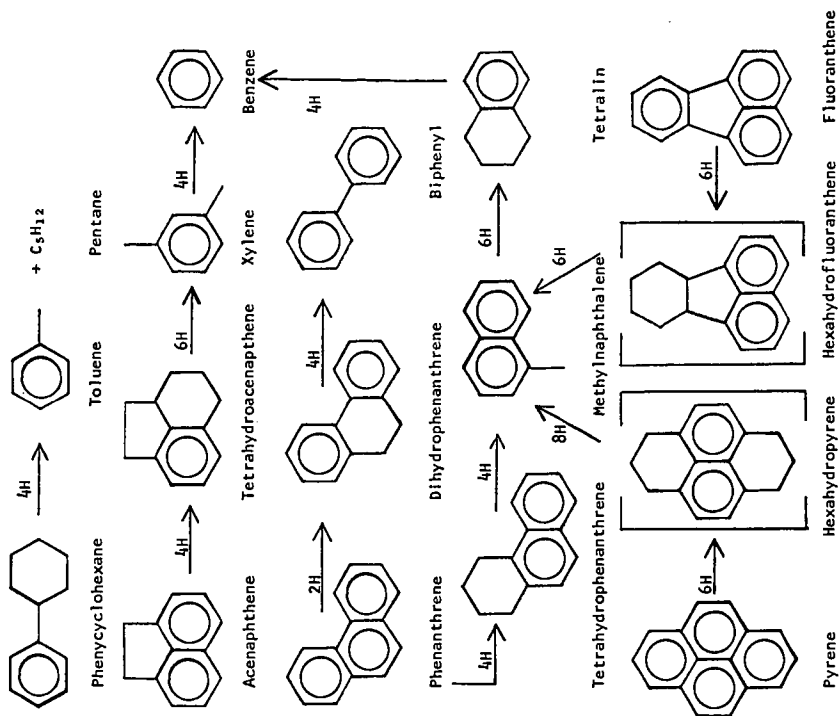
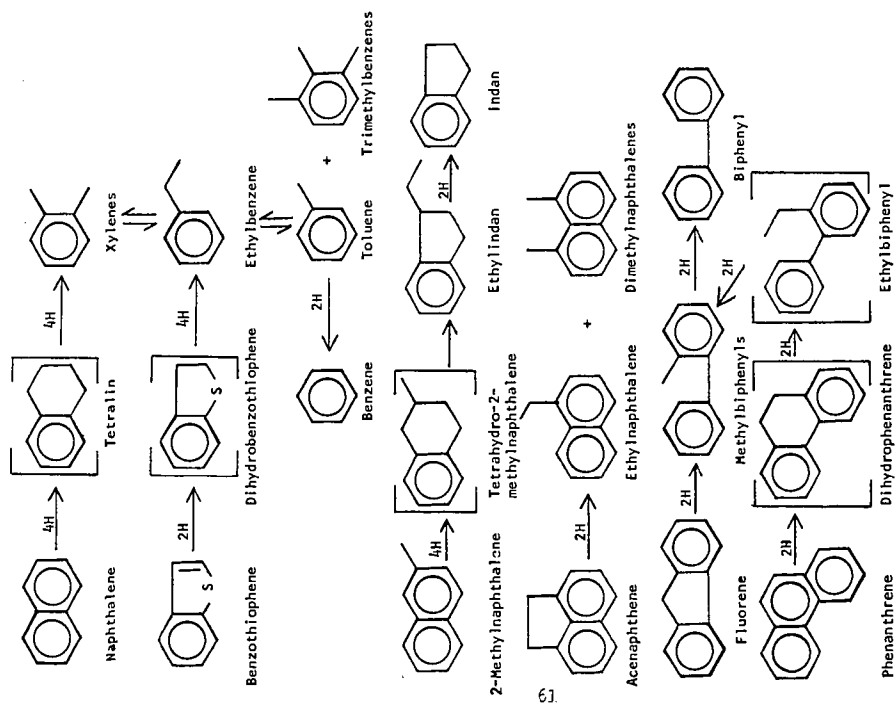


Figure 1. Possible Reaction Mechanisms Involved in Hydrogenation of Tar Oil with Nickel Subsulfide Catalyst at 1,000 psig and 400°C

Figure 2. Possible Reaction Mechanisms Involved in Hydrogenation with Sulfided Nickel-Molybdenum at 400°C and 650 to 1,400 psig